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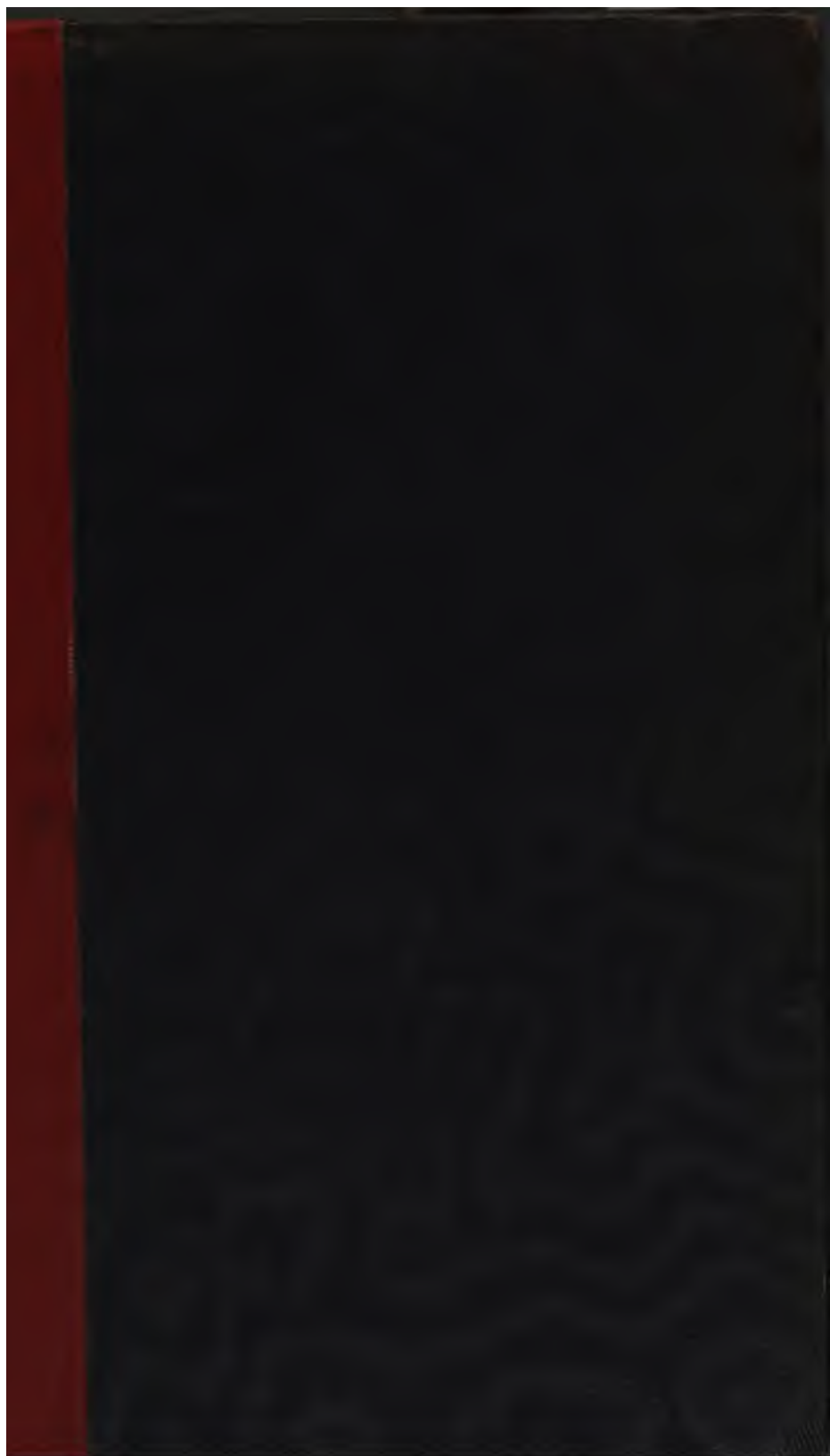
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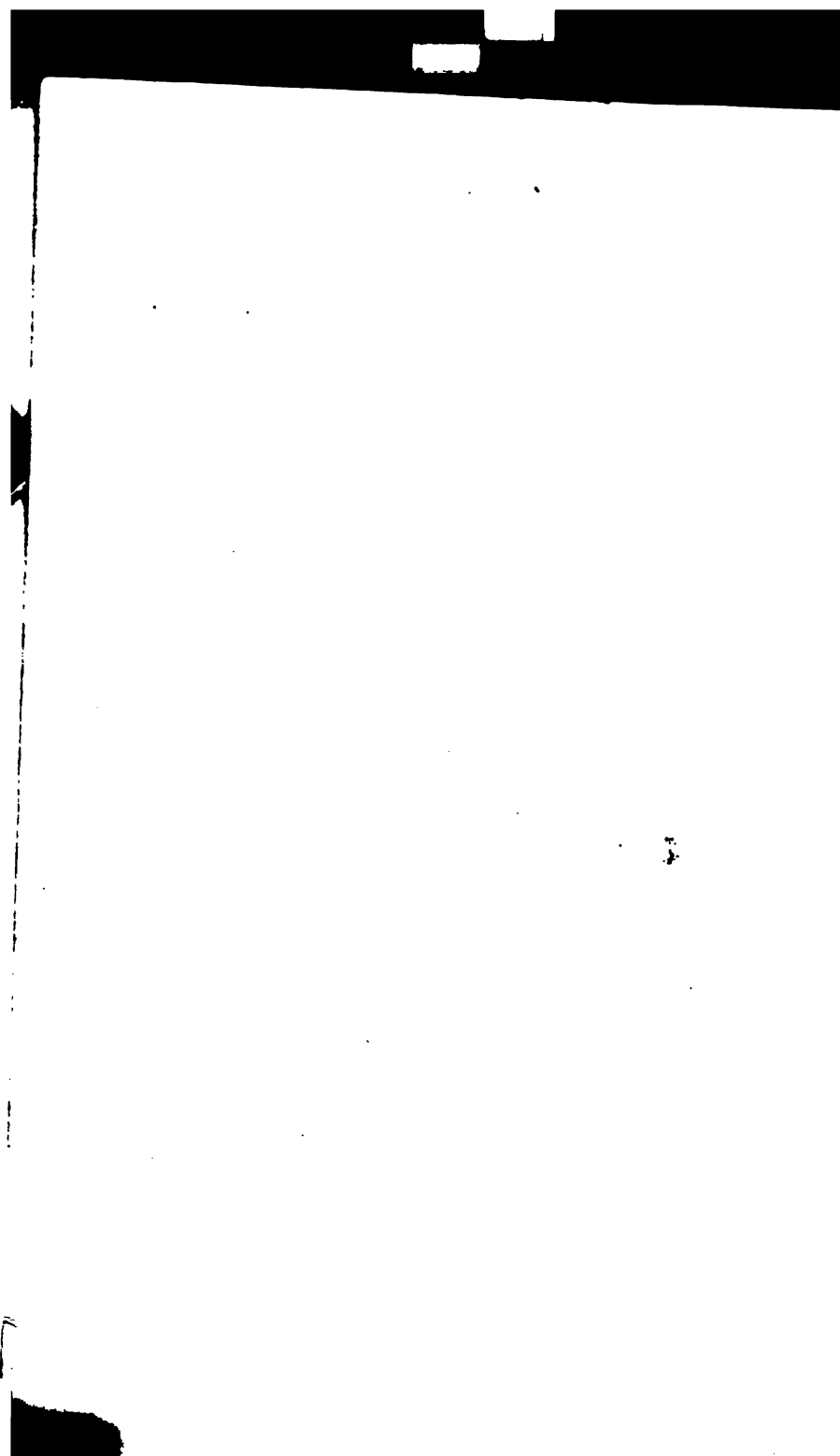
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CONTENTS.

VOL. LXXII.

No. 477.—July 8, 1903.

	Page
Preliminary Note on the Use of Chloroform in the Preparation of Vaccine. By Alan B. Green, M.A., M.D. (Cantab.). Communicated by W. H. Power, M.D., F.R.S.	1
The Combination of Hydrogen and Chlorine under the Influence of Light. By P. V. Bevan, Trinity College, Cambridge. Communicated by Professor J. J. Thomson, F.R.S. (Abstract)	5
A New Class of Organo-Tin Compounds containing Halogens. By William J. Pope, F.R.S., Professor of Chemistry, Municipal School, Manchester, and Stanley J. Peachey	7
On the Photo-electric Discharge from Metallic Surfaces in different Gases. By W. Mansergh Varley, M.Sc. (Vict.), Ph.D. (Strasburg), 1851 Exhibition Research Scholar, Emmanuel College, Cambridge. Communicated by Professor J. J. Thomson, F.R.S. (Abstract)	11
Meteorological Observations obtained by the Use of Kites off the West Coast of Scotland, 1902. By W. N. Shaw, Sc.D., F.R.S., and W. H. Dines, B.A. (Abstract)	13
On the Radiation of Helium and Mercury in a Magnetic Field. By Professor Andrew Gray, F.R.S., and Walter Stewart, D.Sc., with Robert A. Houston, M.A., and D. B. McQuistan, M.A., Research Students in the University of Glasgow	16
An Analysis of the Results from the Kew Magnetographs on Quiet Days during the Eleven Years 1890—1900, with a Discussion of certain Phenomena in the Absolute Observations. By Charles Chree, Sc.D., LL.D., F.R.S., Superintendent of the Observatory Department. (Abstract)	22
On the Theory of Refraction in Gases. By George W. Walker, M.A., A.R.C.Sc., Fellow of Trinity College, Cambridge. Communicated by Professor J. J. Thomson, F.R.S. (Abstract)	24
Researches on Tetanus.—Preliminary Communication. By Professor H. Meyer and Dr. F. Ransom. Communicated by Professor E. H. Starling, F.R.S.	26
The Hydrolysis of Fats <i>in vitro</i> by means of Steapsin. By Dr. J. Lewkowitch and Dr. J. J. R. Macleod, Mackinnon Scholar. Communicated by Professor E. Divers, F.R.S.	31
On the Adaptation of the Pancreas to different Foodstuffs.—Preliminary Communication. By F. A. Bainbridge, M.B., M.R.C.P. Communicated by Professor E. H. Starling, F.R.S.	35
On the Bending of Waves round a Spherical Obstacle. By Lord Rayleigh, F.R.S.	40

	Page
Sur la Diffraction des Ondes Electriques : à propos d'un Article de M. Macdonald. Par H. Poincaré, For. Mem. R.S.....	45
The Measurement of Tissue Fluid in Man.—Preliminary Note. By George Oliver, M.D., F.R.C.P. Communicated by Sir Lauder Brunton, F.R.S.	52
On Reptilian Remains from the Trias of Elgin. By G. A. Boulenger, F.R.S. (Abstract).....	55
The Bending of Electric Waves round a Conducting Obstacle : Amended Result. By H. M. Macdonald, M.A., F.R.S.....	59
On the Structure of Gold Leaf and the Absorption Spectrum of Gold. By J. W. Mallet, F.R.S., Professor of Chemistry in the University of Virginia. (Abstract)	66

No. 478.—July 31, 1903.

Note on the Effect of Extreme Cold on the Emanations of Radium. By Sir William Crookes, F.R.S., and Professor James Dewar, F.R.S.	69
The Evaporation of Water in a Current of Air. By Edgar Philip Perman, Assistant Lecturer in the University College of South Wales and Monmouthshire. Communicated by Professor E. H. Griffiths, F.R.S.	75
The Spectra of Neon, Krypton, and Xenon. By E. C. C. Baly, Lecturer on Spectroscopy in University College, London. Communicated by Sir William Ramsay, K.C.B., F.R.S. (Abstract) ...	84
On a Remarkable Effect produced by the Momentary Relief of Great Pressure. By J. Y. Buchanan, F.R.S. (Plates 1 and 2)	86
The Bionomics of <i>Convolvulus Roscoffensis</i> , with special Reference to its Green Cells. By F. W. Gamble, D.Sc., Owens College, Manchester, and Frederick Keeble, M.A., University College, Reading. Communicated by Professor S. J. Hickson, F.R.S.	92
A Method for the Investigation of Fossils by Serial Sections. By W. J. Sollas, D.Sc., LL.D., F.R.S., Professor of Geology and Palæontology in the University of Oxford. (Abstract)	96
An Account of the Devonian Fish, <i>Palæospondylus Gunni</i> , Traquair. By W. J. Sollas, D.Sc., LL.D., F.R.S., Professor of Geology and Palæontology in the University of Oxford, and Igera B. J. Sollas, B.Sc., Lecturer in Zoology, Newnham College, Cambridge. (Abstract)	98
On the Optical Activity of the Nucleic Acid of the Thymus Gland. By Arthur Gamgee, M.D., LL.D., F.R.S., Emeritus Professor of Physiology in the Owens College, Victoria University, and Walter Jones, Ph.D., Associate Professor of Physiological Chemistry in the Johns Hopkins University	104
New Investigations into the Reduction Phenomena of Animals and Plants.—Preliminary Communication. By J. B. Farmer, F.R.S., and J. E. S. Moore, A.R.C.S.	104
Evolution of the Colour-Pattern and Orthogenetic Variation in certain Mexican Species of Lizards, with Adaptation to their Surroundings. By Hans Gadon, F.R.S. (Plates 3—5).....	108

	Page
Upon the Bactericidal Action of some Ultra-violet Radiations as produced by the Continuous-Current Arc. By J. E. Barnard and H. de R. Morgan. Communicated by Sir Henry Roscoe, F.R.S.....	126
On the Propagation of Tremors over the Surface of an Elastic Solid. By Horace Lamb, F.R.S. (Abstract).....	128
Some Preliminary Observations on the Assimilation of Carbon Monoxide by Green Plants. By W. B. Bottomley, Professor of Botany, King's College, London, and Herbert Jackson, Assistant Professor of Chemistry, King's College, London. Communicated by Professor J. Reynolds Green, Sc.D., F.R.S.	130

No. 479.—August 14, 1903.

The Forces Acting on a Charged Condenser moving through Space. By Professor F. T. Trouton, F.R.S., and H. R. Noble, B.Sc., University College, London. (Abstract)	132
On the Synthesis of Fats accompanying Absorption from the Intestine. By Benjamin Moore, M.A., D.Sc., Johnston Professor of Biochemistry at University College, Liverpool. Communicated by Professor C. S. Sherrington, F.R.S.....	134
Observations on the Physiology of the Cerebral Cortex of the Anthropoid Apes. By A. S. F. Grünbaum, M.D., F.R.C.P., and C. S. Sherrington, M.A., M.D., F.R.S.....	152 ✓
Separation of Solids in the Surface-layers of Solutions and "Suspensions" (Observations on Surface-membranes, Bubbles, Emulsions, and Mechanical Coagulation).—Preliminary Account. By W. Ramsden, M.A., M.D., Oxon., Fellow of Pembroke College, Oxford. Communicated by Professor F. Gotch, F.R.S.	156
The Xanthophyll Group of Yellow Colouring Matters. By C. A. Schunck. Communicated by Horace T. Brown, F.R.S. (Plates 6 and 7)	165
On the Determination of Specific Heats, especially at Low Temperatures. By H. E. Schmitz, M.A., B.Sc. Communicated by Arthur Schuster, F.R.S.	177
The Elasmometer, a New Interferential Form of Elasticity Apparatus. By A. E. H. Tutton, F.R.S. (Abstract)	193

No. 480.—August 15, 1903.

On the Spectrum of the Spontaneous Luminous Radiation of Radium at Ordinary Temperatures. By Sir William Huggins, K.C.B., O.M., D.C.L., Pres. R.S., and Lady Huggins. (Plate 8)	196
On the Oxidising Action of the Rays from Radium Bromide as shown by the Decomposition of Iodoform. By W. B. Hardy, F.R.S., Caius College, Cambridge, and Miss E. G. Willcock, Newnham College, Cambridge	200
Experiments in Radio-activity, and the Production of Helium from Radium. By Sir William Ramsay, K.C.B., F.R.S., and Frederick Soddy, M.A.	204

	Page
On the Intensely Penetrating Rays of Radium. By Hon. R. J. Strutt, Fellow of Trinity College, Cambridge. Communicated by Lord Rayleigh, F.R.S.	208

No. 481.—August 31, 1903.

On the Formation of Definite Figures by the Deposition of Dust. By J. Aitken, F.R.S. (Abstract)	211
Mean Results of Monthly Determinations of the Magnetic Elements at the Valencia Observatory, Cahirciveen, lat. 51° 56' N., long. 10° 15' W. By J. E. Cullum	211
On the Measurement of the Diffusion of Salts in Solution. By J. C. Graham. Communicated by Professor W. E. Ayrton, F.R.S.	212
Surface Flow in Crystalline Solids under Mechanical Disturbance. By G. T. Beilby. Communicated by F. H. Neville, F.R.S. (Plates 9 and 10)	218
The Effects of Heat and of Solvents on Thin Films of Metal. By G. T. Beilby. Communicated by F. H. Neville, F.R.S. (Plates 11—13)....	226
The "Hunting" of Alternating-Current Machines. By Bertram Hopkinson, M.A. Communicated by Professor J. A. Ewing, F.R.S.	235

No. 482.—October 19, 1903.

The Spectra of Metallic Arcs in an Exhausted Globe. By A. Fowler, A.R.C.Sc., F.R.A.S., and Howard Payn, F.R.A.S. Communicated by Sir Norman Lockyer, K.C.B., LL.D., F.R.S. (Plate 14)	253
The Phenomena of Luminosity and their possible Correlation with Radio-Activity. By Professor Henry E. Armstrong, F.R.S., and T. Martin Lowry, D.Sc.	258
Radiation in the Solar System: its Effect on Temperature and its Pressure on Small Bodies. By J. H. Poynting, Sc.D., F.R.S., Professor of Physics in the University of Birmingham. (Abstract)....	265
The Theory of Symmetrical Optical Objectives. By S. D. Chalmers, B.A. (Cantab.), M.A. (Sydney), St. John's College, Cambridge. Communicated by Professor Larmor, Sec. R.S.	267
On the Discharge of Electricity from Hot Platinum. By Harold A. Wilson, D.Sc., B.A., Fellow of Trinity College, Cambridge. Communicated by C. T. R. Wilson, F.R.S. (Abstract)	272
The Properties of the Aluminium-Tin Alloys. By W. Carrick Anderson, M.A., D.Sc., and George Lean, B.Sc. Communicated by Professor H. A. Miers, F.R.S. (Plate 15)	277
Cyanogenesis of Plants. Part III.—On Phaseolunatin, the Cyanogenetic Glucoside of <i>Phaseolus lunatus</i> . By Wyndham R. Dunstan, M.A., F.R.S., Director of the Imperial Institute, South Kensington, and Thomas A. Henry, D.Sc. (Lond.)	285
The Differential Invariants of Space. By Professor A. R. Forsyth, Sc.D., LL.D., F.R.S. (Abstract)	294
The Ultra-violet Spectrum of Radium. By Sir William Crookes, F.R.S. (Plates 16—18)	295

No. 483.—October 31, 1903.

Page

- On the Physiological Action of the Poison of the Hydrophidæ. Part II.
—Action on the Circulatory, Respiratory, and Nervous Systems. By
Leonard Rogers, M.D., B.S. (Lond.), M.R.C.P., F.R.C.S., I.M.S., late
acting Professor of Pathology, Medical College, Calcutta. Communi-
cated by Dr. A. D. Waller, F.R.S. 305

- The Action of Choline, Neurine, Muscarine, and Betaine on isolated
Nerve and upon the excised Heart. By A. D. Waller, M.D., F.R.S.,
and S. C. M. Sowton 320

- The Physiological Action of Betaine extracted from Raw Beet-Sugar.
By A. D. Waller, M.D., F.R.S., and R. H. Aders Plimmer, D.Sc.
(Grocers' Research Student, Jenner Institute of Preventive Medicine) 345

- Note on the Disintegration of Rabid Brain Substance. By J. O. Wakelin
Barratt, Research Student, Jenner Institute of Preventive Medicine.
Communicated by Lord Lister, O.M., F.R.S. 353

- On the Effect of Temperature on Carbon-Dioxide Assimilation. By
Gabrielle L. C. Matthæi. Communicated by F. Darwin, F.R.S.
(Abstract) 355

- An Experimental Investigation of the *Rôle* of the Blood Fluids in con-
nection with Phagocytosis. By A. E. Wright, M.D., late Professor
of Pathology, Army Medical School, Netley, Pathologist to St. Mary's
Hospital, W., and Stewart R. Douglas, M.R.C.S., Captain, Indian
Medical Service. Communicated by Sir John Burdon Sanderson,
Bart., F.R.S. 357

No. 484.—November 21, 1903.

- The Magnetic Expansion of some of the less Magnetic Metals. By
P. E. Shaw, B.A., D.Sc. Communicated by Professor J. H.
Poynting, F.R.S. 370

- On the Measurement of the Pressure Coefficient of Oxygen, at Constant
Volume, and different Initial Pressures. By Walter Makower, B.Sc.,
and Henry R. Noble, B.Sc. Communicated by Sir William Ramsay,
K.C.B., F.R.S. 379

- The Vapour Pressures of Liquid Oxygen on the Scale of the Constant-
volume Oxygen Thermometer filled at different Initial Pressures.
By Morris W. Travers, D.Sc., Fellow of University College, London,
and Charles J. Fox, B.Sc., Ph.D. Communicated by Sir William
Ramsay, K.C.B., F.R.S. 386

- On an Approximate Solution for the Bending of a Beam of Rectangular
Cross-section under any System of Load.—Additional Note. By
L. N. G. Filon, M.A., D.Sc. Communicated by Dr. C. Chree,
F.R.S. 391

- On the Sensation of Light produced by Radium Rays and its Relation
to the Visual Purple. By W. B. Hardy, F.R.S., Caius College,
Cambridge, and H. K. Anderson, M.D., Caius College, Cambridge.... 393

- The Maximum Order of an Irreducible Covariant of a System of
Binary Forms. By A. Young, M.A., Clare College, Cambridge.
Communicated by Major P. A. MacMahon, D.Sc., F.R.S. 399

- The Cell Structure of the Cyanophyceæ.—Preliminary Paper. By
Harold Wager. Communicated by D. H. Scott, M.A., Ph.D., F.R.S. 401

Further Observations on the Spectrum of the Spontaneous Luminous Radiation of Radium at Ordinary Temperatures. By Sir William Huggins, K.C.B., O.M., D.C.L., Pres. R.S., and Lady Huggins, Hon. Mem. R.A.S. (Plate 19)	Pa 46
Correction to Paper "On the Spectrum of Radium." By Sir W. Crookes, F.R.S.	41

No. 485.—December 19, 1903.

On the Rapidity of the Nervous Impulse in Tall and Short Individuals. By N. H. Alcock, M.D. Communicated by A. D. Waller, M.D., F.R.S.	41
On the Physiological Action and Antidotes of Colubrine and Viperine Snake Venoms. By Leonard Rogers, M.D., B.S., M.R.C.P., F.R.C.S., Indian Medical Service. Communicated by A. D. Waller, M.D., F.R.S. (Abstract)	41
Croonian Lecture.—The Cosmical Function of the Green Plant. By C. Timiriazeff, Professor of Botany in the University of Moscow. Communicated by Sir M. Foster, Sec. R.S. (Plates 20—22).....	42

No. 486.—December 29, 1903.

On the Nematocysts of <i>Æolids</i> . By G. H. Grosvenor, B.A., New College, Oxford. Communicated by Professor W. F. R. Weldon, F.R.S.	46
On the Fructification of <i>Neuropteris heterophylla</i> , Brongniart. By Robert Kidston, F.R.S., L. and E., F.G.S. (Abstract)	48
Histological Studies on Cerebral Localisation. By Alfred W. Campbell, M.D. Communicated by Professor C. S. Sherrington, F.R.S. (Abstract)	48
On the Integrals of the Squares of Ellipsoidal Surface Harmonic Functions. By G. H. Darwin, F.R.S., Plumian Professor and Fellow of Trinity College, Cambridge. (Abstract)	49
Preliminary Note on the Resistance to Heat of <i>B. anthracis</i> . By A. Mallock, F.R.S., and Lieut.-Col. A. M. Davies, R.A.M.C.	49
On the Resemblances Exhibited between the Cells of Malignant Growths in Man and those of Normal Reproductive Tissues. By J. Bretland Farmer, F.R.S., J. E. S. Moore, F.L.S., and C. E. Walker	49

No. 487.—January 29, 1904.

Mathematical Contributions to the Theory of Evolution. XII.—On a Generalised Theory of Alternative Inheritance, with Special Reference to Mendel's Laws. By Karl Pearson, F.R.S. (Abstract)	50
Index	51

PROCEEDINGS

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“Preliminary Note on the Use of Chloroform in the Preparation of Vaccine.” By ALAN B. GREEN, M.A., M.D. (Cantab). Communicated by W. H. POWER, M.D., F.R.S. Received April 16,—Read April 30, 1903.

(From the Government Lymph Laboratories.)

It is well known that glycerine exerts an action on vaccine whereby the extraneous bacteria are eliminated in the course of a few weeks, while the specific germ undergoes no undue deterioration from the process.

I have found that by the use of a solution of chloroform in distilled water, the extraneous bacteria of vaccine are eliminated in from one to six hours, the specific germ remaining fully potent for vaccination.

The solution of chloroform that can most advantageously be employed in the preparation of vaccine is a saturated solution in distilled water, having a strength of 1 in 200. This is the limit of such solubility.

The following method of using such solution has so far given the best results :—

Vaccine emulsion is first prepared by triturating vaccine pulp with distilled water. *The presence of the water is essential*, in order that later chloroform may enter into solution with it. About three parts by weight of water should be mixed with one part by weight of pulp. Should a more viscid emulsion of vaccine be desired, glycerine may be added without interfering with the action of the chloroform. I have found that the usual admixture of one part by weight of vaccine pulp and four parts by weight of a solution consisting of equal parts by weight of glycerine and water forms a perfectly suitable emulsion for this process. But glycerine is incapable of dissolving chloroform, and the elimination of extraneous bacteria by this chloroform process

is solely due to the action of chloroform water. Indeed, when addition of glycerine to the vaccine emulsion is desired, it can be very advantageously effected after the completion of this process.

The newly-made vaccine emulsion, to be subjected to the action of chloroform, is dealt with in the following way:—Sterile air is first passed through pure liquid chloroform, whereby this air becomes charged with chloroform vapour. This mixture of air and chloroform vapour is then passed through the vaccine emulsion, which is contained in a cylindrical glass vessel of test-tube shape, and in size suitable to the quantity of vaccine to be treated.

The mixed chloroform vapour and air can be passed seriatim through a number of tubes of vaccine before it finally escapes into the outside air, and it is efficient for all of them, provided that the current be sufficiently strong to keep the contents of each tube in active movement, and that a distinct smell of chloroform be apparent at the outlet of the last tube of the series.

It is essential that no liquid chloroform be allowed to pass over into the vaccine, as its presence is strongly inimical to the potency of the lymph. To obviate the chance of such an accident an overflow bottle, weighted with sterile sand, is interposed between the bottle of liquid chloroform and the tube or tubes of vaccine emulsion.

By passage through it of chloroform vapour and air, the water of the vaccine emulsion quickly becomes saturated with chloroform, and this strength of solution is maintained so long as such passage is continued. When saturation is reached all excess of chloroform immediately escapes automatically from the vaccine. Thus the vaccine is not at any time brought into contact with a stronger solution of chloroform than 1 in 200 in water.

A rapid and marked germicidal action is exerted on the non-spore-bearing extraneous bacteria of vaccine thus treated. The extraneous bacteria most commonly found in vaccines at the Government laboratories are *Staphylococcus pyogenes aureus*, *Staphylococcus pyogenes albus*, *Staphylococcus cereus flavus*, *Staphylococcus cereus albus*. Others which occur either in smaller numbers or less commonly are *Staphylococcus pyogenes citreus*, *Proteus vulgaris*, *Streptococcus pyogenes*, *Sarcina lutea*, and some yeasts. Emulsions, which have contained as many as 100,000 extraneous micro-organisms per platinum loopful at the time of mixture, have, by the action of chloroform water, become free from their presence in from 1—6 hours. This freedom is evidenced by absence of bacterial growth in aërobic and anaërobic plate cultures. The germicidal action is first exerted on the least resistant members of each species of organism present in the vaccine. Generally after the first hour or hour and a half of the process, a very few of the more resistant staphylococci—*aureus* and *albus*—remain alive; these give rise to small inhibited colonies in plate cultures. And these

organisms succumb in their turn after further application of the process.

By contrast, elimination in like degree of the extraneous micro-organisms of vaccine by the glycerine process rarely occurs before the fourth week after mixture, and is frequently not complete until a much later period, as shown by similar plate cultures.

After elimination of extraneous bacteria from chloroformed vaccines, the chloroform is evaporated until no trace remains. Such evaporation is most quickly effected by passing a stream of sterile air through the emulsion.

By the above method vaccine can be brought under the influence of the germicide for such time only as suffices to kill the extraneous micro-organisms. At present, however, there is no evidence to show that more prolonged contact with 1 in 200 watery chloroform solution has any harmful effect on its potency.

As in the case of glycerine, non-spore-bearing bacteria in vaccine lymph are alone killed by this process. But in some thousands of vaccines examined at the Government Lymph Laboratories, the only spore-bearing organisms found in vaccine were the strictly non-pathogenic organisms of the mesenteric group—*Bacillus mesentericus vulgaris*, *Bacillus mesentericus fuscus*, *Bacillus mesentericus ruber*, *Bacillus subtilis*—and equally non-pathogenic moulds such as *Penicillium glaucum*.

The practical working value of the foregoing method has been clearly shown by results of vaccinations performed with vaccines which have been thus subjected to the action of chloroform. These vaccines, having been rendered free from extraneous micro-organisms, were first tested on calves and found to give excellent results. Within a fortnight after collection from the calf and of subjection to the action of chloroform water, such vaccines have been used (after evaporation from them of all chloroform) for primary vaccinations and re-vaccinations with results of high "case" and "insertion" success.

It would seem, therefore, that the following considerable advantages are to be gained by the use of the chloroform process :—

(a) So speedy an elimination of extraneous micro-organisms is attained that vaccine, practically free from such organisms, can be distributed for use within a few hours of its collection from the calf. In times of urgent demand for large quantities of vaccine, such as occur during small-pox epidemics, this process must needs prove of great value, since the necessity for wasting some weeks for elimination of extraneous organisms by glycerine will be done away with.

(b) In so far as the vaccination value of vaccine depends on the activity of a living organism, deterioration of that value must occur in the course of a longer or shorter time. The potency of some vaccines, glycerinated or otherwise, becomes greatly impaired within

4      *Use of Chloroform in the Preparation of Vaccine.* [Apr. 16,

a few weeks of collection, that is within the time required for glycerine to exert fully its influence in eliminating extraneous organisms. Some of these vaccines may, at the time of their collection, have possessed a high vaccination value. Vaccine, characterised by this high but somewhat transient potency, can, by means of the chloroform process, be used at once, before its activity has deteriorated, thus allowing greater economy of vaccine material than would otherwise be possible.

(c) For a similar reason the chloroform process might be of considerable use in hot climates where the preservation of the potency of vaccine is frequently a matter of considerable difficulty.

Experiments are at present being made to test the duration of the potency of chloroformed vaccines. A further account of this process will be given in the Report for 1902—1903 of the Medical Officer of the Local Government Board.

In conclusion I wish to express my indebtedness and thanks to Dr. F. R. Blaxall for the generous help and advice he has given me. My thanks are likewise due to Mr. H. S. Fremlin, with whom I am also associated in the work of these laboratories, and to Mr. S. D. Rowland, of the Jenner Institute of Preventive Medicine, for the help he has afforded me.

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"The Combination of Hydrogen and Chlorine under the Influence of Light." By P. V. BEVAN, Trinity College, Cambridge. Communicated by Professor J. J. THOMSON, F.R.S. Received April 1,—Read May 14, 1903.

(Abstract.)

The present investigation was undertaken primarily to study the initial expansion observed when light is allowed to fall on a mixture of hydrogen and chlorine. This expansion was first noticed by Draper and studied more carefully by Pringsheim. The latter writer attributed the expansion to a dissociation of  $H_2$  and  $Cl_2$  molecules giving rise to a larger number of systems in the gas mixture than before illumination. For this part of the investigation the apparatus invented by Bunsen and Roscoe for determining the actinic properties of light was used. Bulbs considerably larger than Bunsen and Roscoe's were employed, admitting of more accurate determinations of small changes of volume. The expansion was found to be due to a rise in temperature, caused by the combination of hydrogen and chlorine to form hydrochloric acid. This rise in temperature was measured by the change of resistance of a fine platinum wire, sealed through the bulb, in which the gas mixture was exposed to light. The rise in temperature in all cases fully accounted for the initial expansion, and the rise in temperature was itself fully accounted for by the heat of formation of the hydrochloric acid produced. The initial expansion is thus shown to be only a side effect in the general case of the induction. The investigation then considers the period of induction. The action is shown to stop almost instantaneously on cutting off the light, so that combination only goes on while the light is continuously acting. The induction period or time in which the velocity of action has not reached its maximum value can be prolonged indefinitely, but its general character remains the same. The combination is made much more rapid by the presence of water vapour, and it seems probable that were the gases perfectly dry no action would take place.

If chlorine be first of all exposed to light, and then mixed with its own volume of hydrogen, the mixture shows a greater readiness to combine than if the chlorine had not been previously illuminated. This property is lost if the chlorine be bubbled through water after the preliminary illumination. Previous illumination of the hydrogen alone is without effect. The first step in the process of combination is thus an action between chlorine and water vapour or an action on chlorine alone. Some evidence as to the formation of an intermediate body is afforded by the production of a nucleus-forming substance in chlorine alone, and in the mixture of hydrogen and chlorine on which

a cloud can condense when the gas is submitted to a certain expansion. This cloud-forming substance appears before any hydrochloric acid is formed, and thus appears to be due to a true intermediate body.

The induction period, or period of acceleration of the action, is an essential part of the combination, and is to be attributed to the formation of intermediate compounds from water vapour and the two reacting gases. The nature of these compounds is not discovered, but the view is taken that they are molecular aggregates in which the individual atoms can come into each other's spheres of influence and so make intra-aggregate systems without much action on the whole individual, which can then break up, giving rise to the more stable systems, water and hydrochloric acid. This view of the process of the action can be shown to involve the qualitative characteristics of the initial stages of this particular action, and can be extended to actions in gaseous systems when the presence of a catalyser such as water vapour is necessary for the progress of the action at a finite rate. In the case of such actions a period of induction must be expected to occur, and the application of the law of mass action must be made with reference to the intermediate compounds formed with the catalyser. There is, therefore, no reason to expect that agreement will be found between the theory of mass action, as applied to the end-product equations, and the actual experimental results.

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"A New Class of Organo-Tin Compounds containing Halogens."

By WILLIAM J. POPE, F.R.S., Professor of Chemistry,  
Municipal School, Manchester, and STANLEY J. PEACHEY.

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(From the Chemical Laboratories, Municipal School of Technology, Manchester.)

Most of the organo-tin compounds which have hitherto been described may be regarded as derived from the hypothetical stannimethane,  $\text{Sn H}_4$ , and, adopting a nomenclature based upon the name of this substance, the simple types of known organo-tin compounds may be described as the tetralkylstannimethanes, the trialkylstannimethyl chlorides, bromides and iodides, and the dialkylstannimethylene chlorides, bromides and iodides. The analogy between the various classes of derivatives of stannimethane and of methane is as yet incomplete in that no organo-tin compounds corresponding in constitution to chloroform, bromoform and iodoform have been described; methods for preparing such derivatives are, however, given in the present paper, so that the analogy of constitution existing between the corresponding classes of alkyl and halogen compounds of carbon and tin is shown to be complete, and of the kind illustrated by the following table.

|                                       |                           |                                        |                                 |
|---------------------------------------|---------------------------|----------------------------------------|---------------------------------|
| $\text{C}(\text{CH}_3)_4$ .           | Tetramethylmethane.       | $\text{Sn}(\text{CH}_3)_4$ .           | Tetramethylstannimethylmethane. |
| $\text{C}(\text{CH}_3)_3\text{I}$ .   | Trimethylmethyl iodide.   | $\text{Sn}(\text{CH}_3)_3\text{I}$ .   | Trimethylstannimethyl iodide.   |
| $\text{C}(\text{CH}_3)_2\text{I}_2$ . | Dimethylmethylene iodide. | $\text{Sn}(\text{CH}_3)_2\text{I}_2$ . | Dimethylstannimethylene iodide. |
| $\text{C}(\text{CH}_3)\text{I}_3$ .   | Methyliodoform.           | $\text{Sn}(\text{CH}_3)\text{I}_3$ .   | Methylstanniodoform.            |
| $\text{CI}_4$ .                       | Carbon tetriodide.        | $\text{SnI}_4$ .                       | Stannic iodide.                 |
| $\text{CH}_3\text{CO.OH}$ .           | Acetic acid.              | $\text{CH}_3\text{SnO.OH}$ .           | Methylstannoxylic acid.         |

*Methylstanniodoform,  $\text{CH}_3\text{SnI}_3$ .*

Since tetramethylstannimethane is acted upon by iodine with production of trimethylstannimethyl iodide and methyl iodide in accordance with the following equation—



it seemed not unlikely that, on replacing the iodine by stannic iodide, the reaction would take the course indicated by the following equation—



This was found to be the case.

On warming a mixture of tetramethylstannimethane (two parts) and stannic iodide (seven parts) on the water bath, the iodide rapidly dissolves



and, after a few hours standing at the ordinary temperature, methylstanniodoform crystallises in large straw-coloured prisms; the separation of the latter is rendered more complete by the addition of petroleum ether, and, after filtration, the stanniodoform derivative is purified by crystallisation from ether or light petroleum. It crystallises in long needles or prisms closely resembling iodoform in colour and melts at  $82-84^{\circ}$ ; it gradually volatilises at  $100^{\circ}$  and, when slowly heated, distils without decomposition. It is odourless and dissolves very readily in alcohol, acetone and benzene. The following analytical results were obtained :—

0.3083 gave 0.0254  $\text{CO}_2$  and 0.0172  $\text{H}_2\text{O}$ . C = 2.24. H = 0.62.  
0.2964 required  $17.5 \times 0.0169 \text{ AgNO}_3$  for titration. I = 74.4.

Theory for  $\text{Sn}(\text{CH}_3)_3\text{I}$ . C = 2.33. H = 0.58. I = 74.0.

*Methylstannoxylic Acid,  $\text{CH}_3\text{SnO.OH}$ .*

Methylstanniodoform is insoluble in cold water, but dissolves in boiling water giving a solution from which the iodoform derivative cannot subsequently be crystallised; as this behaviour should be attributable to the occurrence of hydrolysis in the following sense,  $\text{CH}_3\text{SnI}_3 + 3\text{H}_2\text{O} = \text{CH}_3\text{Sn}(\text{OH})_3 + 3\text{HI}$ , methylstanniodoform was evaporated on the water bath with an aqueous solution of three molecular proportions of soda; as evaporation proceeded a white precipitate of methylstannoxylic acid was deposited, the reaction being represented by the following equation :—



After washing with water, solution in acetic acid and precipitation with ammonia, the substance gave the following analytical results :—

0.3887 gave 0.0990  $\text{CO}_2$  and 0.0822  $\text{H}_2\text{O}$  and 0.3532  $\text{SnO}_2$ . C = 6.94.  
H = 2.36. Sn = 71.60.

0.3396 gave 0.0869  $\text{CO}_2$ , 0.0800  $\text{H}_2\text{O}$  and 0.3024  $\text{SnO}_2$ . C = 6.97.  
H = 2.63. Sn = 70.16.

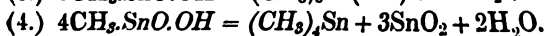
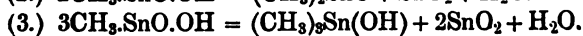
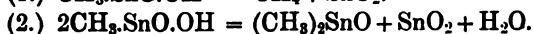
$\text{CH}_3\text{SnOOH}$  requires C = 7.18. H = 2.41. Sn = 71.24.

By the action of methyl iodide on sodium stannite, G. Meyer\* obtained a white powder in which he made one determination of tin, and which he considered to be probably the acid which we now describe. On repeating Meyer's preparation we found that the substance obtained is identical with the methylstannoxylic acid prepared from methylstanniodoform. To the very scanty description given by Meyer we would add the following.

The acid is conveniently prepared by dissolving stannous chloride

\* 'Berichte,' vol. 16, p. 1439.

(100 grams) in the minimum quantity of water, and adding concentrated caustic soda solution until the precipitate formed at first just redissolves. To the solution thus obtained (300 c.c.), absolute alcohol (200 c.c.) and methyl iodide (90 grams) are added; the liquid becomes warm and, after two days repose at the ordinary temperature, is saturated with carbon dioxide, filtered and evaporated on the water bath. During the evaporation, methylstannoxylic acid separates in white crystalline crusts and is obtained in a practically pure condition after filtration and washing with boiling water. The acid is insoluble in water and the ordinary organic solvents, but dissolves slowly in boiling acetic and formic acids. On adding ammonia to the acetic acid solution after dilution with water, no precipitate forms, but on boiling, methylstannoxylic acid separates in a state of purity; the fact that no precipitate occurs until the solution is boiled, indicates the existence in solution of an ortho-acid  $\text{CH}_3\text{Sn}(\text{OH})_3$ , which is only decomposed on heating. Methylstannoxylic acid decomposes slowly at  $120-130^\circ$ , but no volatile tin compound is evolved; on rapid heating it chars and, when ignited, smoulders leaving a residue of stannic oxide. On boiling the acid with dilute caustic potash the greater part dissolves, but the solution never becomes quite clear; when the acid is boiled with stronger potash solution, a rapid evolution of methane occurs, a sublimate of trimethylstannic alcohol,  $(\text{CH}_3)_3\text{Sn.OH}$ , forms and the solution is afterwards found to contain dimethylstannimethylene oxide  $(\text{CH}_3)_2\text{SnO}$ . Lastly, on mixing the acid with solid potash and heating, after the addition of a small quantity of water, methane containing a considerable proportion of tetramethylstannimethane is given off; the latter substance was identified by freezing it out of the gas and determining its boiling point and behaviour towards iodine. The fact that methylstannoxylic acid is not wholly soluble in dilute potash is attributable to a part of it being decomposed with evolution of methane and production of stannic oxide which remains undissolved by the potash. The evolution of methane which attends the heating of methylstannoxylic acid with potash, is quite analogous to the decomposition which occurs when sodium acetate is heated with soda-lime, whilst the formation of dimethylstannimethylene oxide is analogous to the production of acetone by heating calcium acetate; it is, however, difficult to find analogies for the formation of trimethylstannimethyl alcohol and tetramethylstannimethane during the heating of the stannoxylic acid with potash. The four kinds of change would seem to take place in accordance with the following equations:—



Equation (2) is similar to that suggested by Pfeiffer,\* in order to explain the fact that he obtained diethylstannimethylene oxide instead of ethylstannoxylic acid by the action of ethyl iodide on sodium stannate.

A number of attempts were made to prepare salts of methylstannoxylic acid, but these have been uniformly unsuccessful owing to the very feebly marked acidic characters of the substance. The acidic properties of methylstannoxylic acid are, in fact, so very slight that the substance tends to react in the ortho-form rather than in the stannoxylic condition, although the reverse is true in the case of carboxylic acids. Thus, on treating methylstannoxylic acid with concentrated hydriodic acid, it is immediately converted into methylstanniodoform, so that the reaction, by means of which we first prepared the acid, is a reversible one; since methylstannoxylic acid is very easily prepared in quantity by the action of methyl iodide on alcoholic sodium stannite solution, the most convenient method of preparing the stanniodoform derivative consists in treating methylstannoxylic acid with strong hydriodic acid, and, after filtration, crystallising the product from a mixture of benzene and light petroleum.

*Methylstannibromoform, CH<sub>3</sub>.SnBr<sub>3</sub>.*

Methylstannoxylic acid dissolves readily in concentrated hydrobromic acid, and on extracting the solution with light petroleum and evaporating the solvent, methylstannibromoform separates. After crystallisation from petroleum it is obtained in the form of long colourless prisms which melt at 50—55° and may be distilled without decomposing. The substance fumes slightly in the air and dissolves to a clear solution in water. Methylstannibromoform is readily soluble in the ordinary organic solvents. The following analytical results were obtained:—

0.4664 gave 0.0563 CO<sub>2</sub> and 0.0382 H<sub>2</sub>O. C = 3.29. H = 0.91.

CH<sub>3</sub>.SnBr<sub>3</sub> requires C = 3.21 and H = 0.80.

*Methylstannichloroform, CH<sub>3</sub>.SnCl<sub>3</sub>.*

Methylstannoxylic acid dissolves in concentrated hydrochloric acid with evolution of heat, and, after saturating the solution with anhydrous calcium chloride and extracting with benzene, the benzene solution yields a residue when evaporated which slowly crystallises in the desiccator. On gently warming methylstannoxylic acid in a current of dry hydrogen chloride, reaction occurs and methylstannichloroform distils, condensing in the receiver as a colourless crystalline material.

\* 'Berichte,' vol. 35, p. 3503.

The same product is formed on treating the acid with phosphorus trichloride. Methylstannichloroform crystallises from light petroleum in long colourless prisms melting at 105—107° and distils without decomposition at 179—180°. It fumes in the air, dissolves to a clear solution in water, and is very soluble in the ordinary organic solvents.

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"On the Photo-electric Discharge from Metallic Surfaces in different Gases." By W. MANSERGH VARLEY, M.Sc. (Vict.), Ph.D. (Strasbourg), 1851 Exhibition Research Scholar, Emmanuel College, Cambridge. Communicated by Professor J. J. THOMSON, F.R.S. Received April 24,—Read May 14, 1903.

(Abstract.)

The object of the experiments described in this paper was to study as systematically as possible the effect of the pressure and nature of the gas with which a metal surface is surrounded upon the magnitude of the photo-electric current from the surface.

On account of the complicated nature of the relation between the photo-electric current and the potential difference between the electrodes, it is not enough to state, for example, that the current in air at 760 mms. pressure is so many times that in air at 50 mms. pressure, without specifying the exact conditions under which the observations were taken. The method used in these experiments was to draw the complete curves connecting the current and the potential difference at each pressure examined, keeping the intensity of the ultra-violet illumination and the other conditions unaltered.

Great difficulty was encountered in finding a suitable source of ultra-violet light which would remain constant in intensity while long series of observations were being taken, but ultimately the spark between iron terminals in an atmosphere of pure dry hydrogen was found to answer excellently. The spark gap was in parallel with three Leyden jars in the secondary circuit of an induction coil, used as a transformer.

The photo-electric currents were measured from a metal—usually zinc—surface placed a few millimetres behind a fine gauze, through which the light passed, and which served as the positive electrode. A brass vessel, with a quartz window to admit the light, served to contain the electrodes. It was connected to pump, gauge, &c., so that the pressure or gas could be changed at will.

A second similar apparatus was used as a control for the intensity of the light.

Series of curves were obtained, showing the relation between the photo-electric current and the potential at pressures ranging from 760 mm. to 0.0014 mm. They show that at pressures above about 1 mm.—the actual pressure depends on the distance between the electrodes—the current increases at first rapidly with the potential, then less rapidly, and finally, when a certain critical potential gradient has been reached, more rapidly again. No true saturation currents were obtained at these pressures, though the middle portion of the curves were always less steep than the other portions. The currents for the less steep part of the curves increased some twentyfold in value as the pressure was reduced from that of the atmosphere down to a pressure of about 1 mm. Below this pressure the current again decreased, and soon perfect saturation currents were obtained, which became smaller as the pressure was further diminished, though approaching a finite limit.

Curves connecting the potentials and corresponding photo-electric currents in air, carbon dioxide, and hydrogen at various pressures, were also obtained. They show that at the higher pressures the currents in carbon dioxide are about 1.75 times those in hydrogen, and 1.3 times those in air, for corresponding points on the less steep portions of the current potential curves. For the upper part of the curve, when we have ionisation by collision becoming the predominant factor, the relation between the currents is quite altered.

The curves obtained could, however, all be explained on the ionic theory of conduction both qualitatively and quantitatively.

Experiments were also carried out, and the corresponding curves drawn, for the photo-electric currents in carbon monoxide, and for the currents using other electrodes than zinc; the results obtained are given at length in the paper.

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"Meteorological Observations obtained by the Use of Kites off the West Coast of Scotland, 1902." By W. N. SHAW, Sc.D., F.R.S., and W. H. DINES, B.A. Received April 28,—Read May 14, 1903.

(Abstract.)

The paper presents the results of the first organised attempt to obtain a series of automatic records of temperature and humidity in the upper air of the British Isles, or neighbouring seas, by means of kites. They are derived from the records of forty kite ascents, in which instruments were raised, and which were carried out by Mr. Dines and his two sons, under the auspices of the Royal Meteorological Society in co-operation with a committee of the British Association, during the months of July and August, 1902. Two of the ascents were from a small island in Crinan Bay, Argyllshire, the remainder from the deck of a tug steaming in the Jura Sound or neighbouring sea. Kites were raised on seventy-one occasions, but, on thirty-one of them, the force of the wind, even when assisted by the speed of the tug at seven knots, was not sufficient to raise the recording instruments. On those occasions an experimental form of registering air thermometer alone was carried. The average recorded height of ascents with instruments was 5900 feet (1940 metres), and average computed height of the seventy-one ascents 4200 feet (1400 metres); a height of 12,000 feet (3700 metres) was passed on two occasions, and 15,000 feet (4500 metres) was reached once, but the record was lost owing to the breaking away of the highest kite.

The kites and winding gear were designed and constructed by Mr. Dines. Particulars are given in the Quarterly Journal of the Royal Meteorological Society, vol. 29, p. 65, 1903.

The average angular elevation given by the kites with a short length of line was  $62^{\circ} 30'$ , the greatest height reached with one kite was 5500 feet (1700 metres), with two 9200 feet (2800 metres), with three 12,400 feet (3800 metres).

The method of dealing with the records is described and illustrated. The results are expressed on a diagram representing, by a series of points and connecting lines, the height in the air of a series of temperatures with successive intervals of  $1^{\circ}$  C. for each ascent. The diagram thus presents a set of isothermal lines referred to time and height as co-ordinates. So far as the observations extend, the changes in the actual and relative positions of the lines show how the temperature varied at the surface and in the upper air during the period of the experiments.

On account of the unsatisfactory nature of the hygrometric records,

only four stages of humidity are dealt with, and these are entered upon the diagram, upon which are also recorded the observed heights of clouds entered by the kites, the direction of the wind at the surface and in the upper air, and particulars of the weather.

For the purpose of comparison the curves of variation of the barometer at Fort William and Ben Nevis, during the period of the experiments, are plotted on the same diagram, and certain particulars are also given about the temperatures of the wet and dry bulb at those stations.

From the diagram the fall of temperature for each 500 metres of each ascent is taken out and tabulated. The table gives the following average results.

Table of Fall of Temperature in Degrees Centigrade for each  
500 Metres of Ascent.

|                 |      |   | July.      |        | August.    |        |
|-----------------|------|---|------------|--------|------------|--------|
| 0 to 500 metres |      |   | 22 ascents | 3.0 C. | 13 ascents | 2.6 C. |
| 500             | 1000 | " | 16         | "      | 11         | "      |
| 1000            | 1500 | " | 9          | "      | 9          | "      |
| 1500            | 2000 | " | 2          | "      | 7          | "      |
| 2000            | 2500 | " | 1 ascent   | 2.0    | 3          | "      |
| 2500            | 3000 | " | —          | —      | 2          | "      |
| 3000            | 3500 | " | —          | —      | 2          | "      |

The range of fall for the first 500 metres varied from 4° C. to 1° C. The smallest fall was associated with an inversion of temperature gradient not far from the surface. An inversion of temperature gradient with very dry air above a layer of clouds was shown also on one of the occasions of steepest gradient near the surface. The steep gradients observed in the lower strata are shown to be associated with anti-cyclonic conditions preceding the approach of a depression, and by examples on five occasions it is shown that the characteristic of the passage of a depression is that the isothermal lines of the diagram open out as the depression comes on, the average diminution of gradient for the change of barometric condition amounting to as much as 50 per cent.

The paths of the centres of depressions producing these changes are shown on the maps taken from the monthly weather reports of the Meteorological Office. It appears that they passed the station on all sides at various distances but none actually crossed it. The results show that whatever was the path taken by the centre, the column of air over Crinan became relatively much more nearly uniform in temperature under the influence of the depression, and therefore probably represented a relatively warm column of air.

The average of the values of temperature gradient in columns of

air of different heights derived from all the Crinan ascents are as follows :—

| Height of column.<br>Metres. | Temperature gradient.<br>Per 100 metres. |
|------------------------------|------------------------------------------|
| 500                          | 0.56                                     |
| 1000                         | 0.56                                     |
| 1500                         | 0.52                                     |
| 2000                         | 0.50                                     |
| 2500                         | 0.48                                     |
| 3000                         | 0.46                                     |
| 3500                         | 0.43                                     |

It must be remembered that a moderately strong wind was required for the higher ascents, and they therefore refer to a more or less special type of weather. The gradients for the higher columns are accordingly not so generally applicable as those for the lower columns.

The results are compared with temperature gradients observed elsewhere as given in Hann's "*Meteorologie*," with the theoretical temperature gradient in dry air ( $1^{\circ}$  C. per 100 metres), and with that for saturated air having an initial temperature  $12^{\circ}$  C. The last differs but little from  $0.53^{\circ}$  C. per 100 metres for all ranges up to 2000 metres and then increases. The average Crinan gradient is almost identical with this and with the conventional correction in use in this country for the reduction of temperatures to a common level, viz.,  $1^{\circ}$  F. per 300 feet.

The last part of the paper is devoted to considering the differences between the temperatures as observed in the free air at the same height as the summit of Ben Nevis and those read on the mountain itself. The differences are always in favour of the free air, which is shown to be on the average  $2.6^{\circ}$  warmer than the mountain summit. Various circumstances are adduced to support the result, and an explanation is sought in the suggestion that the air flowing from the sea over the mountain would be mechanically raised and practically subject to the adiabatic gradient which is not reached in the free air. The consideration of the relative heights of clouds as observed on the hill sides and over the sea is adduced in corroboration.

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“On the Radiation of Helium and Mercury in a Magnetic Field.”

By Professor ANDREW GRAY, F.R.S., and WALTER STEWART, D.Sc., with ROBERT A. HOUSTOUN, M.A., and D. B. MCQUISTAN, M.A., Research Students in the University of Glasgow. Received April 27,—Read May 14, 1903.

The experiments described in the following paper had for their primary object to test, for as many lines as possible of different substances, the proportionality of the change  $d\lambda$  of wave-length, for each of the components into which a single spectral line is resolved by the application of a magnetic field, to the field intensity  $H$ , and to deduce the corresponding values of the ratio  $e/m$  of charge to mass of the electron. It has been found difficult to obtain a ready supply of good discharge-tubes, and up to the present our observations have been mainly of the spectra of helium and mercury, in the latter case chiefly of the green line of wave-length approximately 5461 tenth-metres.

With respect to this line we incidentally observed fully a year ago, as we found afterwards had also been done a little earlier by Zeeman,\* that in its immediate neighbourhood there existed a number of comparatively faint lines, so that what appeared in an ordinary spectroscope as a single bright line was in fact a group of six or seven, consisting of one bright line with a triplet of faint satellites on the side next the violet end of the spectrum, and a triplet or at least a doublet of faint lines on the other side. These faint lines were very difficult to observe and to determine, and the measurements of wave-lengths which we obtained do not agree with those supplied to Zeeman by MM. Fabry and Perot.\* The lines, however, we found were only visible in our tubes, when the discharge had been kept going for a long time, and when, therefore, the vacuum had been considerably changed; and from glimpses that were obtained at times of what seemed to be further lines, it appears probable that the full complexity of the green line, when unaffected by a magnetic field, has not yet been disclosed, and can only be investigated under peculiar conditions of the vacuum in the tube, and possibly of the action of the discharging coil. An important question is raised by these facts as to what it is that is resolved by a magnetic field; it may not be correct to regard the complex of lines, which are plainly seen when a powerful field is applied to this light, as a resolution of the simple central line. It will be convenient to defer further particulars of these observations until after a short description of the apparatus employed.

\* ‘Astrophysical Journal,’ vol. 15 (1902), p. 220.

*Apparatus.*

*Electro-magnet.*—The apparatus consisted of a set composed of a large electromagnet and an echelon spectroscope of twenty-six plates with auxiliary. The magnet was specially made for the purpose of these experiments and some others. The iron part (yoke, limbs and poles), is rectangular in form, and is about three feet long by about a foot and a quarter deep. The permeability of the cast-steel used for the yoke and limbs coincides very nearly with that given by Hopkinson for wrought iron: for  $H = 35$  C.G.S. the value of  $B$  is 15,000 C.G.S. A large magnetising coil surrounds the yoke and extends over its whole length. The poles are provided with smaller coils about a foot in length, having respectively 1140 and 1170 turns of copper wire of No. 9 standard wire gauge. The coils can stand easily about 16 ampères, and for short periods 50 or 60 ampères. The field intensity between the poles, as tested by the usual ballistic method, is exceedingly great; but unfortunately we have not hitherto been able to observe the Zeeman effect in a field of much higher intensity than 10,000 C.G.S., as in all the tubes with which we have worked the light becomes so faint at the higher fields that it is not possible to obtain readings.

*The Echelon.*—The echelon, which is by Hilger, London, has twenty-six plates; the thickness of each is 10.23 mm.; the width of step is 1 mm. The difference in wave-length between two lines under observation is given by

$$d\lambda = \frac{\lambda^2}{\left\{ \mu - 1 - \lambda \frac{d\mu}{d\lambda} \right\} \delta} \frac{d\phi_1}{d\phi_2},$$

where  $d\phi_1$  is the angular displacement between the two lines  $\lambda, \lambda + d\lambda$ ,  $d\phi_2$  that between two successive orders of spectrum,  $\delta$  the thickness of one of the echelon plates, and  $\mu$  the refractive index of the glass for wave-length  $\lambda$ . We have always determined the ratio  $d\phi_1/d\phi_2$  by means of a micrometer eye-piece fitted to the observing telescope.

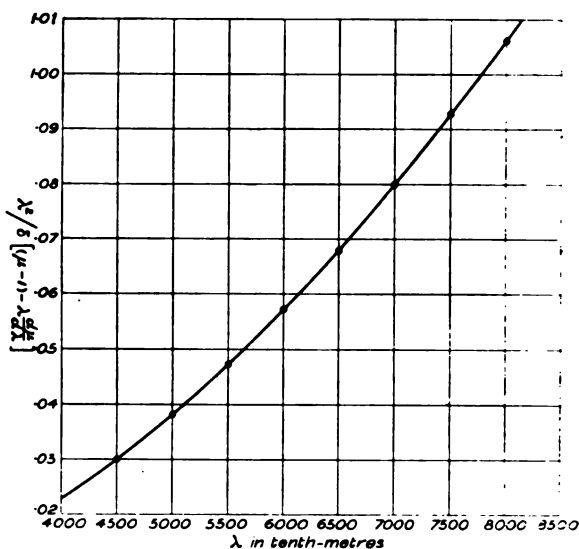
The factor, which multiplies  $d\phi_1/d\phi_2$ , was obtained in the following manner. The refractive index of the glass,  $\mu$ , was given by the maker of the instrument for the four lines C, D, F, G. For D it is 1.5746. Cauchy's relation between refractive index and wave-length was assumed, namely,

$$\mu = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4},$$

and in this equation were substituted for  $\mu$  and  $\lambda$  their known values for three of the principal wave-lengths, giving three simultaneous equations to determine the three constants  $A, B, C$ . It was verified that these values of  $A, B, C$  gave to less than a unit in the fourth place of decimals the values of  $\mu$  furnished by the makers for the four

lines C, D, F, G. Then from Cauchy's equation were calculated values of  $\mu$  corresponding to the wave-lengths 4000, 4500, 5000, 5500 and so on up to 8000 tenth-metres. From these values a curve was plotted which gave  $\mu$  for any wave-length. In a similar manner a curve was plotted which gave  $-\lambda d\mu/d\lambda$  for any value  $\lambda$ . Finally we calculated a sufficient number of values of the multiplying factor  $\lambda^2/(\mu - 1 - \lambda d\mu/d\lambda) \delta$ , and plotted a curve giving the value of this factor for any wave-length. This curve is shown in fig

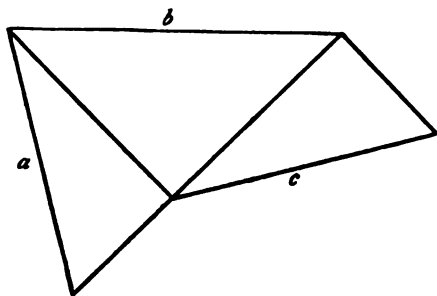
FIG. 1.



*Arrangement of Apparatus.*—The source of light was an exhaust tube, containing the vapour the spectrum of which was under examination, provided as usual with terminals and joined up in the secondary circuit of an induction coil; the capillary part of the tube was placed between the poles of the electromagnet. A convergent lens was placed so as to bring the light from the tube to a focus on the collimator slit of the auxiliary spectroscop, which effected preliminary partial resolution of the light before it fell on the echelon of the collimator used directly with the echelon. This auxiliary spectroscop was of the constant deviation kind, and had the collimator and telescope fixed at right angles to one another. The prism was a species of internal reflection prism, made up of two 30° prisms: one right-angled prism, cemented together as shown in fig. 2. The light entered at the face *a*, underwent internal reflection at the hypotenusal face *b*, and emerged at the face *c*. With this arrangement the part of the spectrum in the middle of the field of view was

to be seen under a dispersion equal to that of a ray passing through a  $60^\circ$  prism in the position of minimum deviation. Any required part of the spectrum could be got into the middle of the field by a rotation of the prism-table. The eye-piece of the observing telescope of this auxiliary spectroscop was removed, and the collimator of the echelon was placed coaxially with that telescope, and at such a distance that the light rays, after passing through the object glass of the telescope, were brought to a focus on the collimator slit of the echelon. After emerging from the lens system of the collimator, the rays passed through the echelon grating, and were viewed by means of a telescope focussed for parallel light. This telescope was provided with a micrometer eye-piece, whose indications, as already stated, gave the ratio  $d\phi_1/d\phi_2$ .

FIG. 2.



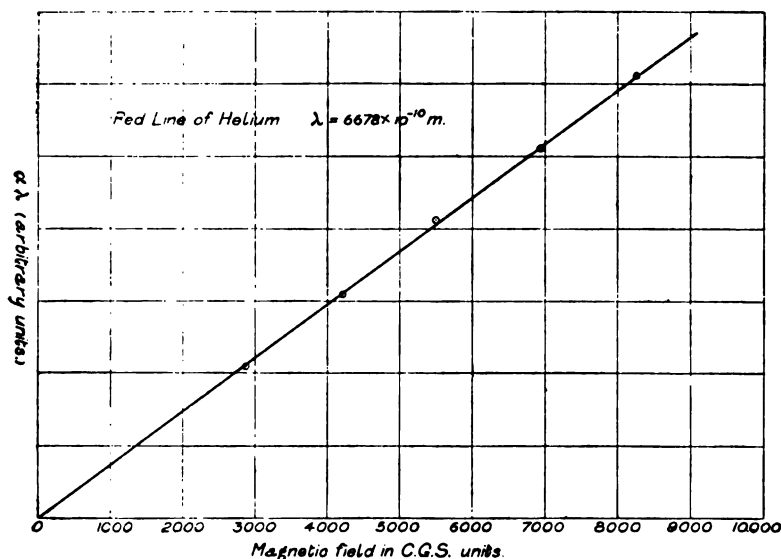
By means of a suitable arrangement the prism-table of the auxiliary spectroscop could be rotated by the observer when taking readings without moving away from his position. In a similar way the width of the echelon slit could be adjusted.

*Results.*—The first observations were made at right angles to the magnetic field on several of the helium lines, and on the green line of mercury. The results were used to calculate the values of  $d\lambda/H\lambda^2$ , and of  $e/m$  by the formula  $e/m = 2\pi v d\lambda/H\lambda^2$ , where  $v$  is the velocity of light,  $3 \times 10^{10}$  cms. per second. In every case the normal triplet was obtained, and the separation between the extreme components found to be proportional to  $H$  up to fields of 10,000 C.G.S., beyond which it was difficult to obtain readings for the reason already stated. The numbers obtained are stated in the following table, and in fig. 3  $\delta\lambda$  is shown plotted against  $H$  for different values of the latter, for the red line of helium. A similarly close proportionality was found in the other cases :—

| Substance.  | Wave-length,<br>$10^{-10}$ cm. | $\delta\lambda$ H.    | $\delta\lambda/H\lambda^2$ . | $e/m$ .              |
|-------------|--------------------------------|-----------------------|------------------------------|----------------------|
| Helium..... | 5016 (green)                   | $1.61 \times 10^{-5}$ | $6.41 \times 10^{-5}$        | $12.1 \times 10^6$ , |
| „ .....     | 5876 (yellow)                  | $2.07 \times 10^{-5}$ | $6.00 \times 10^{-5}$        | $11.3 \times 10^6$ , |
| „ .....     | 6678 (red)                     | $2.90 \times 10^{-5}$ | $6.49 \times 10^{-5}$        | $12.2 \times 10^6$ , |
| Mercury ... | 5461 (green)                   | $2.12 \times 10^{-5}$ | $7.12 \times 10^{-5}$        | $13.4 \times 10^6$ . |

Each result in the above table is the mean of several determinations; of three, seven, and five respectively in the case of helium, and of seven in the case of the mercury line.

FIG. 3.



When, with the green line of mercury under observation, the field strength was increased to 13,000 C.G.S., the centre component of the normal triplet was doubled, while each of the outer components was itself tripled. The polarisation of the two triplets and of the central doublet was the same as that of the lines from which they originated, namely, that of the lines of the normal triplet.

At all fields up to 13,000 the faint companion to the yellow helium line  $D_3$  was not tripled, but only doubled.

For all the lines specified above, observations were made also along the lines of force, one of the magnet cores being replaced for this purpose by a core drilled from end to end with a hole about a centimetre in diameter. The normal doublet was observed up to a field of about 10,000 C.G.S., and the separation between the two

components found to be proportional to the field strength. In this case, however, it was more difficult to obtain reliable results, owing probably to the disturbance of the field produced by the hollow pole. The following table gives the numbers obtained :—

| Substance.    | Wave-length. | $\delta\lambda/H$ .   | $\delta\lambda/H\lambda^2$ . | $e/m$ .              |
|---------------|--------------|-----------------------|------------------------------|----------------------|
| Helium.....   | 5016         | $1.75 \times 10^{-5}$ | $6.95 \times 10^{-5}$        | $13.1 \times 10^6$ , |
| „ .....       | 5876         | $2.24 \times 10^{-5}$ | $6.50 \times 10^{-5}$        | $12.3 \times 10^6$ , |
| „ .....       | 6678         | $3.13 \times 10^{-5}$ | $7.01 \times 10^{-5}$        | $13.2 \times 10^6$ , |
| Mercury ..... | 5461         | $1.88 \times 10^{-5}$ | $6.31 \times 10^{-5}$        | $12.0 \times 10^6$ . |

The results here given for helium are the means of six, seven and five determinations respectively, those for the green line of mercury are the means of eight determinations.

The observations of Zeeman on the green line of mercury, when the field was zero, are referred to above. They followed an observation of Perot and Fabry,\* that the line appeared to be a triplet consisting of the main line with a fainter companion on each side at about the same distance. Our observations gave three companions on the violet side, and two (we seemed at times to see three) on the red side. The values of  $d\lambda$  for these are for the first time  $-0.208$ ,  $-0.096$ ,  $-0.059$ , and for the other two  $+0.032$ ,  $+0.067$ . But, as has been stated, we have had what seem unmistakable indications that this line system is of hitherto unexpected complexity, which is only disclosed under special conditions of the discharge tube. Hence, though these values of  $d\lambda$  do not agree in several cases with those observed by Perot and Fabry, it is not impossible that both sets of observations are correct.

It ought here to be noticed that Runge and Paschen† have obtained a resolution of the green mercury line into three triplets. This observation is entirely confirmed as to the side triplets by ours (which were made before Messrs. Runge and Paschen's paper came to hand), but we have not been able to verify their result for the middle group, which appears to us to be a doublet. But Messrs. Runge and Paschen's instrument was a large Rowland grating of 6.5 metres diameter of circle, and the spectrum was photographed, so that their observations were, no doubt, more certain than ours.

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\* 'Comptes Rendus,' vol. 126 (1898), p. 409.

† 'Astrophysical Journal,' vol. 15 (1902), p. 235.

“An Analysis of the Results from the Kew Magnetographs on *Quiet Days* during the Eleven Years 1890—1900, with a Discussion of certain Phenomena in the Absolute Observations.” By CHARLES CHREE, Sc.D., LL.D., F.R.S., Superintendent of the Observatory Department. Received May 1, —Read May 28, 1903.

(From the National Physical Laboratory.)

(Abstract.)

The late Kew Observatory Committee joined in 1890 in a scheme, whereby five days each month were to be selected as magnetically *quiet* days by the Astronomer Royal, with a view to the curves on these days being tabulated by observatories which did not care to undertake the tabulation of every day's curves. That scheme has been persisted in, and the present paper deals with the results it has led to during the eleven years 1890—1900. The paper treats of the secular change in the several elements, of the annual inequality, of the diurnal inequality, and the non-cyclic effect in the diurnal variation. Attention is more particularly given to the declination, inclination, and the horizontal and vertical components, but some consideration is also given to the northerly and westerly components of the horizontal force and to the total force.

Diurnal inequalities are got out for each month of the year in the principal elements. These inequalities are analysed into Fourier's series, and the variation of the Fourier coefficients is traced throughout the year. Attention is also given to the variation throughout the year in the ranges of the diurnal inequalities and in the sum of the twenty-four hourly differences from the mean for the day. The diurnal inequalities are shown graphically in various ways, serving to illustrate different features.

As explained in a “Preliminary Note,” the relations between magnetic phenomena and sun-spot frequencies have been investigated. The present paper treats of this investigation in detail. Attention is given to the ranges, and the sum of the twenty-four hourly differences from the mean of the day in the diurnal inequalities, and to the amplitudes and phase angles of the terms in the Fourier series representing these inequalities. Some of the results obtained for Kew are compared with corresponding results for Wilhelmshaven and Parc St. Maur, based on data given by Borgen and Moureaux. The results from the stations compared showed a very good agreement.

It is found that the non-cyclic effect in the diurnal variation, and the variability in the declination—recently discussed by the

author in connection with the observations of the "Southern Cross" Antarctic Expedition—show a relation to sun-spot frequency similar to that observed in the ranges of the diurnal inequalities themselves.

A comparison is made between magnetic and meteorological phenomena at Kew from two groups of years, the one representing large, the other small sun-spot frequency. This serves to bring out the insignificance of the connection between meteorological phenomena at a given station and sun-spots—if any such connection exists—as compared to the connection between magnetic phenomena and sun-spots.

A comparison is instituted *inter alia* between the variation throughout the year in the amplitude of the Fourier coefficients in the series found for diurnal inequalities of the magnetic elements and atmospheric temperature, making use of temperature data discussed by General Strachey. It is shown that the amplitudes of the twenty-four-hour term in the Fourier series in the two cases vary in a very similar fashion throughout the year, but that this is not true of the twelve-hour, eight-hour, or six-hour terms. Attention is also called to the fact that, in the temperature diurnal inequality, the twenty-four-hour term preponderates in a way that is not found in any of the magnetic elements. The bearing of this is pointed out on theories as to the source of the magnetic diurnal inequality.

Attention is also drawn to a peculiarity in the variation from month to month in sun-spot frequencies, which enables a somewhat searching inquiry to be made as to the simultaneity of changes in sun-spot frequency and magnetic ranges.

A final section deals with the true nature of the connection between sun-spot frequency and magnetic phenomena. A comparison is made between Wolfer's provisional sun-spot frequencies for all days in the year and for the Astronomer Royal's magnetically quiet days. The conclusion come to is, that sun-spot frequency on any particular day is no guide to the magnetically quiet or disturbed character of the day, and that even mean results for a month for sun-spot frequency and magnetic ranges are but slightly related. It is pointed out that the phenomena observed would be consistent with the view that increased sun-spot activity and increased magnetic activity on the earth are due to some common source external to the sun, whose effect at the same instant varies appreciably throughout the solar system. If the source lies in the sun itself, it is concluded either that sun-spots afford no satisfactory quantitative measurement of it, or else that the effect at the earth is influenced by what takes place at the sun during a considerable time. If the source of the magnetic diurnal inequality be, as has been suggested by various physicists, electrical currents generated by the sun's action in the upper atmosphere, the cause of the increase in the amplitude of the in-



equality at times of great sun-spot frequency may be some form of radiation which reduces the resistance of the atmosphere to currents generated by the sun. This would explain the phenomena without requiring the enormous variations in the sun's output of energy from year to year that would appear necessary to account for the great variations in the magnetic phenomena, variations moreover which—as the paper shows—do not appear to be accompanied by any but the most insignificant changes in the amplitude of the temperature inequality at the earth's surface. The importance is pointed out of reliable information as to whether atmospheric electricity potential, at low and at high levels, resembles magnetic phenomena in being largely different in years of large and small sun-spot frequency.

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“On the Theory of Refraction in Gases.” By GEORGE W. WALKER, M.A., A.R.C.Sc., Fellow of Trinity College, Cambridge. Communicated by Professor J. J. THOMSON, F.R.S. Received May 2,—Read May 28, 1903.

(Abstract.)

The present theories of refraction in gases lead to expressions for the refractive index, of which the formula

$$\mu^2 - 1 = Nf(p)$$

may be taken as typical.

In the formula  $\mu$  is the refractive index,  $N$  is the number of molecules per unit volume,  $p$  is the frequency of the waves, and  $f(p)$  is a function of  $p$  which depends on the assumptions made as to the constitution of the molecule.

The formula, although it explains the main features in the visible spectrum, cannot always be made to explain the measured temperature effects, even when allowance is made for the deviations from the gaseous laws of Boyle and Charles.

Again, in the case of the dielectric constant for some gases such as  $\text{SO}_2$  and  $\text{NH}_3$ , the value of  $K - 1$  is much greater than the value of  $\mu^2 - 1$ . In such cases we find that  $\mu^2 - 1$  varies nearly as  $N$ , while  $K - 1$  is more nearly proportional to  $N/\theta$ , where  $\theta$  is the absolute temperature.

The theories are thus inadequate, and a modification is required which will give a greater dependence on temperature.

In the theories of Voigt and Lorentz the molecule is regarded as an aggregate of electrical doublets. The individual parts are assumed to *have free periods* of vibration, which are naturally identified with the

spectral lines of the gas, and, therefore, must have a frequency independent of temperature.

The view adopted in the present paper is that, instead of free vibrations, we have constrained motion. Regarded from Professor J. J. Thomson's point of view, the atom consists of a large positive particle and a large number of small negative ones. Instead of supposing that these negative particles can vibrate radially, I regard them as rolling on the surface of the positive one in constrained motion. The effective control on transmitted waves is thus the rotational energy of motion of the particles, and it must be proportional to the absolute temperature.

When, by collisions or otherwise the rotational motion becomes so great that the electric attraction is overcome by the centrifugal force, ionisation occurs. The frequency or frequencies of rotation at which this occurs are determined by the electrical attractions and are independent of temperature, although, of course, the higher the temperature the greater will be the amount of ionisation. I regard these frequencies as corresponding to the spectral lines, and it will be seen that the view explains the ionisation produced by ultra-violet light, and also agrees with the fact that luminosity is probably always connected with ionisation, *e.g.*, the characteristic lines come out in the electrical discharge through the gas.

Regarded simply as obstacles, the molecules must contribute a term to  $\mu^2 - 1$ , which is proportional to  $N$  and practically independent of the frequency.

The final formula obtained is

$$\mu^2 - 1 = k_1 N + \frac{k_2 N}{\theta} f(p, \theta),$$

where  $k_1$  and  $k_2$  are constants and  $f(p, \theta)$  is a function of  $p$  and  $\theta$ . The function is fully discussed in the paper.

The formula is shown to be capable of accounting for all the known facts connected with the dielectric constant and the refractive index, while the absorption of ultra-violet light and apparent absorption, due to selective reflexion in the infra-red, is also explained.

Notwithstanding the very complex and varied facts in Air, Hydrogen, Carbon Dioxide, Ammonia and Sulphur Dioxide, complete numerical agreement between the measurements of  $K - 1$  and  $\mu^2 - 1$ , as regards both absolute magnitude and dependence on pressure, temperature and frequency, has been established.

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“Researches on Tetanus.—Preliminary Communication.” By—  
Professor HANS MEYER and Dr. F. RANSOM. Communicated  
by Professor E. H. STARLING, F.R.S. Received May 7,—  
Read May 28, 1903.

(From the Pharmacological Laboratory of the University of Marburg.)

In the following communication we propose to give shortly the results of a series of experiments carried out with the object of throwing light upon certain points in the etiology of tetanus.

In the first place we directed our attention to so-called *local tetanus*, for which an experimental explanation was hitherto wanting.

Our observations led us further to a satisfactory interpretation of the *period of incubation*; to the discovery of a form of tetanus, confined to the sensory system, which we have called *tetanus dolorosus*; to a *theory of the action of tetanus toxine* and, finally, to a definition of the sphere within which the *serum treatment* of tetanus is effectual.

### I.—*Local Tetanus.*

*Gumprecht*, in attempting an explanation of local tetanus, arrived *per exclusionem* at the conviction that the toxine is carried to the nervous centres by the nerve lymphatics, and *Marie*, also without positive proof, adopted the same theory. On the other hand, *Courmont* and *Doyon* and especially *Brunner* discussed, but did not accept this idea.

We have, as we believe, succeeded in demonstrating that the transport of tetanus toxine to the central nervous system takes place only *by way of the motor nerves*.

The experimental proof of this statement is as follows:—

1. Toxine was found in the *motor nerve* after subcutaneous injection in a hind leg. This result has been confirmed by *Marie* and *Morax*.
2. The endangered spinal centres can be protected, if the passage of toxine along the motor nerve be blocked by means of anti-toxine injected into the substance of the nerve. This holds good as well when the toxine has been injected locally as when it has been introduced direct into the blood.
3. If a lethal dose of tetanus toxine be injected into the n. ischiadicus of a cat, the first symptom is a local tetanus of the muscles of the injected limb. This is followed *seriatim*, after a certain period during which the other hind leg is usually attacked, by tetanus of the trunk, fore legs, muscles of the neck. Such a progression of the disease from the hinder to the front part of an animal can, under certain conditions, be prevented by *section of the spinal cord*.
4. A dose of toxine which, if introduced under the skin, causes no,

or but slight, symptoms, is often sufficient to produce death if injected into a motor nerve.

5. Even when the blood contains a large quantity of anti-toxine it is still possible to produce tetanus by injecting toxine into a motor nerve, although, under similar circumstances, subcutaneous or intravenous injections calls forth no symptoms whatever.

## II.—*The Period of Incubation.*

If the path of the toxine is centripetal along the motor nerve, we should expect that injection direct into the substance of the nerve trunk would shorten the period of incubation.

If it were possible to introduce the toxine at once into the neighbourhood of the susceptible centres of the spinal nervous system, this shortening ought to be still more marked.

Both these anticipations are strikingly confirmed by our experiments. We are, therefore, of opinion that the greater part of the *period of incubation* is the expression of the time occupied in the conveyance of the toxine from the periphery along the motor nerves to the susceptible centres.

The results of our injections of toxine into the spinal cord are furthermore of great interest in that they prove that not only the exaggeration of the reflexes, but also the so characteristic *tetanic rigidity* of the muscles is due to the action of the toxine on the *nervous centres to the entire exclusion of the periphery.*

## III.—*Tetanus Dolorosus.*

In all our experiments with injection of tetanus toxine into the substance of the spinal cord we observed, as the first symptom of intoxication, an extremely remarkable sensory disturbance which remained strictly localised, even when the muscular rigidity and the exaggeration of the reflexes were becoming general. In several cases, indeed, this sensory disturbance was so great as to lead to death, apparently from exhaustion, before the ordinary symptoms of tetanus were clearly developed.

Briefly, this symptom consisted in *extreme hyperæsthesia* of some part of the periphery corresponding to the spinal centre into which the injection had been made. This over-irritability of the pain-reflex apparatus is certainly due to the action of the toxine and is quite apart from the ordinary tactile-motor reflex tetanus. It never occurs after simple subcutaneous or intravenous administration of the toxine, nor after injection into a nerve trunk. On the other hand, if the toxine be introduced direct into a *posterior root* the result is pure *tetanus dolorosus*, thus indicating that the spinal ganglion forms an *insuperable obstacle* to the transport of the toxine.

The reflex answer to the attacks of pain consists in co-ordinated defence movements, *i.e.*, brain reflexes.

We draw from these experiments the following conclusions :—

1. The tetanus toxine never reaches the spinal centres by way of the sensory nerves.
2. The pain apparatus in the spinal cord is so insulated from the motor that an intoxication of the one group never goes over to the other.
3. The actual movement of toxine in the nervous system takes place *not in the lymphatics* but in the *protoplasm of the nerves*.

In the third conclusion is to be found the explanation of the fact that the cerebral tetanus of Roux and Borrel only occurs when the toxine is injected into (or by some lesion can reach) the brain substance. Between the brain and the peripheral nerves enough ganglia are interposed to bar the access of toxine to the convulsion centres.

The occurrence of tetanus dolorosus and cerebral tetanus would alone suffice to show that the toxine does not enter the nerve cells from the blood-lymph stream.

In the course of our researches on tetanus dolorosus we observed a peculiar condition which set in after division of the spinal cord. So soon as the communication with the brain was cut off, the manifestations of pain ceased of course, but, instead, a state of things developed which may be called *jactation tetanus*, the hind legs being kept almost uninterruptedly in jerking movement for hours together, till finally death occurred, apparently from extreme exhaustion.

As long as the pain-impulse could reach the brain there was no sign of this agitation, on the contrary, the animals kept as still as possible, in order to avoid any irritation of the hyperæsthetic area. But, transmission to the brain being prevented, the energy set free by the pain-stimulant discharged itself in the spinal cord, causing these movements, which may be looked upon as the *spinal equivalent* of the central reflex movements of the intact animal.

#### IV.—Behaviour of Tetanus Toxine towards Sensory and Vasomotor Nerves.

Injection of toxine into the infra-orbital nerve did not give rise to any symptoms analogous to tetanus dolorosus, but was once followed, after the quite unusual incubation period of 14 days, by an isolated tetanus of the erector muscles of the ear on the injected side.

Our observations lead us to think that the toxine may possibly be carried centralwards in a sensory nerve, but that sensory disturbance *cannot be caused* in this way.

The injection of toxine into the vagus of dogs was followed, in two cases, by a considerable slowing of the pulse which, in one case, lasted some four weeks. The effect, though small in proportion to the dose, seems to indicate that the heart-retarding centres of the vagus are susceptible to tetanus toxine. Except after injection into the vagus we have never observed slowing of the pulse in tetanised animals.

#### V.—*Exaggerated Reflexes and Muscular Rigidity.*

Our experiments show conclusively that the tonic rigidity of the muscles and the exaggeration of the reflexes are due to entirely different and independent processes. Reflex tetanus is known to be a discontinuous series of contractions of short duration. The tetanic rigidity of the muscles, on the other hand, is a continuous and gradually increasing shortening, which may however regress. This shortening, when it has existed for 24—30 hours, is not affected by curare nor by section of the nerve.

As regards the exaggeration of the reflexes, the experiments demonstrate clearly that this is at first strictly localised in the sensory part of the reflex arc belonging to the rigid limb. It is as if this point in the spinal cord were alone poisoned by strychnine.

#### VI.—*A Theory of Experimental Tetanus Intoxication.*

A consideration of the observed facts has led us to adopt the following explanation of the course of experimental tetanus:—

The toxine is taken up from the point of injection by the motor nerves. Passing along these it reaches first the motor centres in the cord and excites there an *over-irritability*, so that the discharges, which in the norm only give rise to the so-called *muscular tone*, become abnormally strong (though not reaching the maximum at first). The extensors and flexors of the injected limb brace themselves more and more and in the hind limbs the extensors tend to overcome the flexors. This, however, takes place gradually, so that for a considerable time voluntary and reflex movements can be executed. In short it may be said that tetanic rigidity is an *intensified muscular tone in the affected limb*. This tetanic contraction or retraction of the muscles is dependent on sensory excitement only in so far as, according to *Hering*, every motor impulse is peripherogen. At bottom it arises from a *pathological condition* of the *motor apparatus* in the spinal cord.

The excess toxine is next carried in the fibres of the cord to the motor apparatus of the corresponding limb of the other side. After a time, and if enough toxine has been given, the nearest connected *sensory apparatus* of the reflex arc in the spinal cord is attacked, with the result that the *general reflex movements* following irritation of the

injected limb or its nerve are exaggerated, though from all other parts of the body only normal reflexes are excited.

If the intoxication proceeds further the motor tonus, as well as increased reflex irritability spreads, and rigidity of almost all striped muscles and general reflex tetanus set in.

The tetanus of warm-blooded animals consists, in fact, of processes separated from each other both in time and space. Of the one is primary, a motor intoxication: local muscular rigidity; other, secondary, is a local sensory intoxication: a diffused reflex tetanus, starting from the intoxicated neuron.

#### VII.—*The Behaviour of Tetanus Anti-toxine in the Organism.*

We found in repeated experiments that when tetanus toxine introduced direct into a motor nerve, anti-toxine, though present in large quantities in the blood, was unable to prevent the outbreak of the disease or even to hinder a fatal issue. This was the case both when large doses of anti-toxine were given before and after the toxin as well as when an actively immunised animal was employed.

We conclude, therefore, that injected anti-toxine does not reach the substance of the nerve fibrils and centres, and that even with highly immunised animals the neurons remain free from anti-toxine.

On the other hand, it has been shown that the cerebro-spinal fluid, and, therefore, the nerve lymph of an immunised animal contains anti-toxine, there remains, therefore, only the fibril plasma as carrier of the toxine. We are further inclined to think that, in face of the facts revealed by our researches, it is difficult to look upon the nerve system as the source of tetanus anti-toxine.

As regards the value of the serum treatment of tetanus, it is clear from what has been said above, that any toxine which is already in the nerve substance, though not yet in the spinal cord, cannot be reached and neutralised by anti-toxine, whether given under the skin or direct into the blood. An attack corresponding to the amount of toxin absorbed by the nerves will infallibly break out and run its course in spite of the anti-toxine. On the other hand, the toxine still in the blood and lymph will be rendered harmless by an injection of anti-toxine, the absorption of fresh toxine from the infected wound hindered and in this way an otherwise fatal result may be prevented and the life of a tetanus patient saved.

NOTE.—A full report of these researches will appear in Schmiedeberg's 'Archiv f. experiment. Pathologie und Pharmacologie.'

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"The Hydrolysis of Fats *in vitro* by means of Steapsin." By Dr. J. LEWKOWITSCH and Dr. J. J. R. MACLEOD, Mackinnon Scholar. Communicated by Professor E. DIVERS, F.R.S. Received May 11,—Read May 28, 1903.

A few months ago, one of us (J. L.) stated\* that he had made a series of experiments in which lipase was allowed to act on cotton-seed oil, and that he had only been able to obtain hydrolysis amounting to 3 per cent. Dr. Macleod then suggested that it would be of considerable interest to ascertain the extent to which steapsin could carry the hydrolysis under the same conditions. We, therefore, decided to investigate this question conjointly, and we are now in a position to show beyond doubt that steapsin is capable of hydrolysing (saponifying) fats outside the organism to a very great extent. As this fact appears to us of considerable physiological importance, inasmuch as the quantitative experiments have hitherto been made almost entirely on monobutyryl and simple esters,† we publish this preliminary notice without referring to the literature *in extenso*. This will be done after the completion of the experiments we have in hand.

#### *Preparation of the Steapsin Solution.*

The steapsin solutions A and B (see table) were prepared from fresh ox pancreas. The pancreas was freed of fat, minced, and 200 grams ground up in a mortar with water. In the case of preparation A, 0.1 per cent. of mercuric chloride was added, and in B some thymol. The preparations were then digested in the incubator at body temperature for 20 hours.‡ Next they were filtered, and the filtrate examined for steapsin by vigorously shaking 2—3 c.c. in a test tube with a few drops of filtered butter fat, adding a drop of an alcoholic solution of phenolphthalein and then decinormal caustic soda solution, till a deep red colour was obtained. Exactly the same mixture was

\* 'Jour. Soc. Chem. Ind.,' 1903, p. 67.

† Nencki ("Spaltung der Säureester der Fettreihe und der aromatischen Verbindungen im Organismus und durch das Pancreas," 'Arch. für exper. Path. u. Pharmak.,' vol. 20, p. 367) tested the action of an aqueous extract of pancreas on mutton fat, but found hydrolysis to proceed only to about 20 per cent. By adding bile to the digest the saponification amounted to about 60 per cent. Pawlow ('The Work of the Digestive Glands,' translated by W. H. Thompson, London, 1902) also records determinations by Dr. Walther (pp. 29, 39) of the steatolytic action of pancreatic juice obtained from a fistula, but the results do not give us an estimate of the actual amount of hydrolysis effected. They were used by the workers for comparative observations.

‡ These are the methods recommended by Ferd. Klug ("Ueber Gasentwicklung bei Pankreasverdauung," 'Pflüger's Archiv,' vol. 70, p. 329, 1898).



placed into a second test tube, the pancreatic extract having, in this case, been heated to destroy its ferments. The preparations were incubated at 37° C. After about half-an-hour the preparations were examined. In the case of the steatolytically active mixture, the contents of the test tube were found to be discoloured, and the amount of decinormal caustic soda solution necessary to restore the original red tint was ascertained. Preparations C and D were obtained from 200 grams minced, fresh pig pancreas by simply triturating in mortar with twice the bulk of water. In these cases the preparations were not incubated, for it was evident that in the previous experiments with A and B the steapsin had been destroyed, as the preparations, before incubation, were very active steatolytically when tested by the above method, but only very slightly so after incubation; probably this was due to the action of trypsin on steapsin. It was also noticed with preparations A and B that the steapsin remained on the filter paper when the solutions were filtered, the filtrates having much weaker steatolytic powers than the precipitates. Preparations C and D were therefore, only filtered through muslin.

#### *Preparation of the Emulsion of Fat and Steapsin.*

100 grams of cotton-seed oil, or lard, were weighed out and carefully triturated in a mortar with measured quantities of the pancreatic extract. Great care was taken to obtain a complete emulsion. The emulsion was then poured into bottles which were well corked to exclude growth of fungi, and allowed to stand at the ordinary temperature.\* If the temperature was raised too rapidly, say by immersion in a water bath kept at 30° or 35° C, the emulsified mass would separate into two layers, and no hydrolysis would then take place. It is therefore of the greatest importance to carefully observe the mixture for some hours, and to thoroughly shake them up as soon as signs of separation are noticed, in order to restore the state of emulsion. A good plan is to immerse the well-shaken emulsion in cold water, or to let it stand in the open during the night. After a few days, distinct hydrolysis is noticeable. In the case of cotton-seed oil, the outward sign of hydrolysis is the hardening of the mass, due to the fatty acids that have been formed.

#### *Consideration of Results.*

The following table contains a series of observations made on cotton seed oil and lard. The amount of hydrolysis was measured by the percentage of free fatty acids, expressed in terms of oleic acid. The

\* Most of the preparations kept free from infection during the time these experiments lasted. Only a few became covered with growth of *Penicillium glaucum* after the lapse of about four weeks.

experiments with A B and C were started on February 19th, and those with D on March 5th. The first observations were made after a lapse of 4 days. The delay was caused through some of the emulsions having separated into two layers, which necessitated the re-establishing of the state of emulsion by frequent shaking. It will be noticed that in those experiments with cotton-seed oil, in which neither acid nor alkali had been added, hydrolysis had reached after four days, in the case of preparation C, from 22·9 per cent. (No. 5) to 32·8 per cent. (No. 6), and in the case of preparation D, from 31 per cent. (No. 11) to 37·1 per cent. (No. 9). After another 7 days, samples Nos. 11 and 9 had reached 46·3 per cent. and 44·3 per cent. respectively. As it was not expected that further hydrolysis would proceed very rapidly, some time was allowed to elapse before the next tests were taken. It will be seen from the table that the highest percentages of hydrolysis, when neither acid nor alkali was added, were 86·7 per cent. in the case of preparation C (No. 6), and 83·8 per cent. in the case of preparation D (No. 10). In both cases the steapsin had been allowed to act for 56 days. Whereas the experiments made with C show that the amount of hydrolysis increases with the amount of steapsin mixed with the oil, no such striking regularity is apparent in the case of preparations D (Nos. 9 to 11).

Further experiments were made with cotton-seed oil under the same conditions, only with that difference that either dilute acid or dilute caustic soda was added. So far, no decisive influence of either acid or alkali has been noticed, and from the experiments recorded here, no definite conclusions can be drawn.

Curiously enough, the hydrolysis of lard proceeds at a very much slower rate, reaching only about one-third of the hydrolysis noticed in the case of cotton-seed oil. Since the consistency of lard favours the state of emulsion, one would have expected the opposite result. The last two experiments with lard seem to show that an increased amount of caustic soda, whilst favouring hydrolysis at the commencement, seems later on to retard the action of the steapsin, notwithstanding the larger amount of the latter.

The numbers recorded in the table show that the steapsin is not capable of producing the reversible reaction which it was thought, reasoning by analogy, this enzyme might produce.

These preliminary experiments are very interesting from a physiological point of view; they prove for the first time that it can be demonstrated by the usual quantitative methods of fat analysis that steapsin is a very powerful fat-splitting ferment.

We are now investigating the action of steapsin and of lipase on fats, in the presence of bile, small quantities of soaps, and a number of other substances which suggest themselves from a physiological point of view.

| No.                     | Preparation. | Cubic centimetres of preparation per 100 grammes of cotton-seed oil or lard. | Date on which started. | Added to emulsion.           |                           | Percentage of free fatty acids formed. |         |         |                                             |                 |      |  |
|-------------------------|--------------|------------------------------------------------------------------------------|------------------------|------------------------------|---------------------------|----------------------------------------|---------|---------|---------------------------------------------|-----------------|------|--|
|                         |              |                                                                              |                        | Acid.                        | Alkali.                   | Feb. 23.                               | Mar. 2. | Mar. 9. | Mar. 16.                                    | Apr. 16, May 1. |      |  |
| <i>Cotton seed-oil.</i> |              |                                                                              |                        |                              |                           |                                        |         |         |                                             |                 |      |  |
| 1                       | A 1          | 10                                                                           | 19/2/03                | 0                            | 0                         | ..                                     | ..      | 0.95    | Separation into two layers had taken place. |                 |      |  |
| 2                       | A 2          | 20                                                                           | 19/2/03                | 0                            | 0                         | ..                                     | ..      | 0.8     | "                                           |                 |      |  |
| 3                       | A 3          | 16                                                                           | 19/2/03                | 0.5 c.c. of 2 % acetic acid  | 0                         | ..                                     | ..      | 1.14    | "                                           |                 |      |  |
| 4                       | B            | 10                                                                           | 19/2/03                | 0                            | 0                         | ..                                     | ..      | 0.95    | "                                           |                 |      |  |
| 5                       | C 1          | 20                                                                           | 19/2/03                | 0                            | 0                         | ..                                     | ..      | 43.3    | 48.4                                        | 80.6            | ..   |  |
| 6                       | C 2          | 30                                                                           | 19/2/03                | 0                            | 0                         | 22.9                                   | ..      | 49.9    | 60.45                                       | 86.7            | ..   |  |
| 7                       | C 3          | 25                                                                           | 19/2/03                | 0.5 c.c. of 2 % acetic acid  | 0                         | 32.8                                   | ..      | 41.04   | 48.8                                        | 74.7            | ..   |  |
| 8                       | C 4          | 30                                                                           | 19/2/03                | 0                            | 0.5 c.c. 1/10 norm. NaOH  | 10.22                                  | 26.4    | 55.4    | 63.1                                        | ..              | ..   |  |
| 9                       | D 1          | 30                                                                           | 5/3/03                 | 0                            | 0                         | 31.25                                  | 39.5    | 37.1    | 44.3                                        | 68.3            | 70.2 |  |
| 10                      | D 2          | 50                                                                           | 5/3/03                 | 0                            | 0                         | ..                                     | ..      | 32.7    | 46.4                                        | 71.5            | 83.8 |  |
| 11                      | D 3          | 60                                                                           | 5/3/03                 | 0                            | 0                         | ..                                     | ..      | 31.03   | 46.3                                        | 60.8            | 79.5 |  |
| 12                      | D 4          | 60                                                                           | 5/3/03                 | 0.5 c.c. of 2 % acetic acid  | 0                         | ..                                     | ..      | 30.4    | 45.2                                        | 65.3            | 73.7 |  |
| 13                      | D 5          | 60                                                                           | 5/3/03                 | 0                            | 0.5 c.c. 1/10 norm. NaOH  | ..                                     | ..      | 36.5    | 44.9                                        | 66.4            | 73.5 |  |
| 14                      | D 6          | 30                                                                           | 5/3/03                 | 0                            | 1 c.c. 1/10 norm. NaOH .. | ..                                     | ..      | 31.4    | 43.8                                        | 74.1            | 74.3 |  |
| 15                      | D 7          | 50                                                                           | 5/3/03                 | 1 c.c. of 2 % acetic acid .. | 0                         | ..                                     | ..      | 37.66   | 44.5                                        | 65.2            | 77.2 |  |
| <i>Lard.</i>            |              |                                                                              |                        |                              |                           |                                        |         |         |                                             |                 |      |  |
| 16                      | D 8          | 50                                                                           | 5/3/03                 | 0                            | 0.5 c.c. 1/10 norm. NaOH  | ..                                     | ..      | ..      | ..                                          | ..              | ..   |  |

"On the Adaptation of the Pancreas to different Food-stuffs."  
 Preliminary Communication. By F. A. BAINBRIDGE, M.B.,  
 M.R.C.P. Communicated by Professor E. H. STARLING, F.R.S.  
 Received May 25,—Read May 28, 1903.

(From the Physiological Laboratory, University College, London.)

It has been found by Walther and other observers that the chemical composition of pancreatic juice varies in response to the stimulus of different food-stuffs; a fatty diet, for example, led to the secretion of a larger amount of steapsin in the pancreatic juice than did a diet devoid of fat.

Further, Weinland showed that whereas the pancreatic juice of adult dogs normally contained no lactase, the juice of dogs fed for some days on milk contained lactase in large amount.

My experiments have been made in the hope of determining, firstly, whether the pancreas does adapt itself to different food-stuffs, and secondly, by what means this adaptation takes place.

*Method.*—Milk was chosen as a convenient food, which could readily be added to or excluded from the diet; and the enzyme studied was *lactase*, which converts lactose into galactose and dextrose. Dogs were fed on milk, sometimes with the addition of pure lactose, for periods varying from 12—60 days. Then the animals were anæsthetised with morphia and A.C.E. mixture, and the pancreatic juice obtained by means of secretin.

A certain quantity of pure lactose was weighed, and made up to a known volume. Part of this was estimated at once by Pavy's method; to another part pancreatic juice was added, and the mixture incubated at 37° for 18—48 hours, chloroform or toluol being also added to prevent bacterial action; a control experiment was also made.

The solution was then acidified with acetic acid, boiled for several minutes, filtered, made up to a known volume, and estimated by Pavy's method. In each experiment the same solution of Pavy's fluid was employed for estimating the pure lactose, and the solution after incubation, so as to exclude any error due to varying strengths of the Pavy's solution; moreover, the conditions as regards the duration of the boiling of the sugar solutions during estimation, the rate at which the Pavy's fluid was added, and other details were kept as far as possible constant in every experiment. With these precautions, Pavy's method was found to be extremely accurate, and it has the advantage that the reducing power of inverted lactose is very much larger than that of pure lactose. Almost invariably 50 c.c. Pavy's solution were titrated at each observation, and the sugar solutions used for the estimation had a *concentration* of about 0·5 per cent.

The extracts of intestinal mucous membrane were made by scraping the gut after washing away all food debris; the gut was ground with sand, and extracted with chloroform-water, lactose solution, tap-water. The extracts were then filtered through muslin, and either injected at once, or kept in an ice-chest until they were required.

*Results.*—The samples of lactose, galactose, and dextrose which were used, had the following reducing powers on Pavy's solution, taking dextrose as 100.

|                                             |       |
|---------------------------------------------|-------|
| Pure lactose .....                          | 52·0  |
| Lactose inverted with hydrochloric acid ... | 88·5  |
| Pure dextrose .....                         | 100·0 |
| Pure galactose .....                        | 87·4  |

The theoretical value of inverted lactose is therefore 93·7, but we never succeeded in obtaining this figure by even prolonged boiling of lactose with acid.

I. The pancreatic juice was first examined in dogs kept for some days in the laboratory, and fed on biscuits only. In such dogs lactose was never found. The following protocol illustrates a typical experiment :—

*Experiment I.* Dog fed on biscuits only for 2 weeks—

The dog was anaesthetised with morphia and A.C.E. mixture, and pancreatic juice collected by means of secretin.

Pure lactose solution, strength 3·640 per cent.

(a.) 25 c.c. pure lactose solution, diluted to 200 c.c. and titrated.  
10·2 c.c. = 50 c.c. Pavy's solution.

(b.) 25 c.c. lactose solution }  
2 c.c. pancreatic juice } Incubated at 37° for 72 hours.  
Few drops  $\text{CHCl}_3$ ..... }

Neutralised with acetic acid, boiled, filtered, and made up to 200 c.c.

10·4 c.c. = 50 c.c. Pavy's solution.

II. *Dogs fed on milk.*—When dogs were fed on milk, to which lactose was added in some cases, their pancreatic juice invariably contained lactase, and an inversion of lactose, varying from 12—per cent., occurred in different cases. A table of the different experiments and a protocol of one of them illustrates this point :—

TABLE I.—Figures representing the number of c.c. which reduced 50 c.c. Pavy's solution.

| Experiment. | Pure Lactose. | Lactose + Juice (Milk-fed dog). | Degree of Inversion. |
|-------------|---------------|---------------------------------|----------------------|
|             | C.c.          | C.c.                            | Per cent.            |
| I .....     | 11.1          | 10.53                           | 16.3                 |
| II .....    | 14.5          | 12.6                            | 31.6                 |
| III .....   | 8.6           | 7.8                             | 22.6                 |
| IV .....    | 9.65          | 9.05                            | 15.0                 |
| V .....     | 9.4           | 8.8                             | 15.4                 |

*Experiment II.*—Dog fed on milk only for 26 days.

Anæsthetised with morphia and HCl mixture; pancreatic juice collected.

Pure lactose solution = 5.167 per cent.

(a.) 20 c.c. pure lactose solution made up to 200 c.c.

9.4 c.c. = 50 c.c. Pavy's solution

(b.) 20 c.c. lactose solution  
       5 c.c. pancreatic juice } Incubated at 37° for 24 hours.  
       Few drops CHCl<sub>3</sub>..... }

Neutralised, boiled several minutes, filtered, made up to 200 c.c.

8.8 c.c. = 50 c.c. Pavy's solution.

These experiments indicate that when dogs are fed on milk, the pancreas secretes a ferment—lactase—which is capable of inverting milk-sugar, although in dogs *not* fed on milk no such ferment is present in pancreatic juice. It appears, therefore, that the pancreas does adapt itself to different food-stuffs by modifying the composition of its secretion, at any rate as regards the enzymes.

It is believed by Pawlow and others that this adaptation is carried out entirely by a nervous mechanism, and that a given food reflexly excites the pancreas to secrete a juice specially adapted for the digestion of that particular food-stuff. The same view has been adopted by Weinland, as regards the lactase of the pancreas. In the light of Professor Starling's work on "Secretin," however, it seemed much more probable that the adaptation was due to a chemical stimulus.

Since lactase is normally present in the intestinal mucous membrane of adult dogs and is increased in amount by a milk diet, it seemed possible that lactase entered the blood stream from the intestine and was picked out by the pancreas and secreted. But the blood of a milk-fed dog was found to have no inverting action on lactose, nor did intravenous injections of extract of the mucous membrane of the intestines of biscuit-fed dogs cause any secretion of lactase in the

pancreatic juice. Consequently, the lactase of the pancreas is not taken up as such from the blood, but must be formed by the pancreas itself.

Weinland's observation that lactose injected subcutaneously did not cause the formation of lactase by the pancreas, led to the inference that the intestinal mucous membrane must be concerned in the production of lactase. I therefore made secretin from a milk-fed dog and injected it into a biscuit-fed dog, but the pancreatic juice of the latter contained no lactase. Then the intestinal mucous membrane of a biscuit-fed dog was ground up with sand and a strong solution of lactose. After standing for some hours, the fluid was filtered off and injected into a second biscuit-fed dog. Ordinary secretin was also injected and the pancreatic juice collected; it contained no lactase.

The influence of lactase injected into the gut during life was then investigated. A strong solution of lactose was injected into the intestine of a biscuit-fed dog, and after  $1\frac{1}{2}$  hours, secretin was injected, and the pancreatic juice collected and examined; no lactase was present.

The intestinal mucous membrane of this dog was extracted with sand and water, filtered and injected intravenously into a second dog (also biscuit-fed). After waiting  $1\frac{1}{2}$  hours, the pancreatic juice was collected and examined; slight inversion occurred, so that the pancreas had secreted some lactase.

Then the intestinal mucous membrane of a kitten fed only on milk was extracted and intravenously injected into a dog; after two hours the pancreatic juice was collected and found to contain lactase, as the following figures show:—

|                                                                                      |          |                                 |
|--------------------------------------------------------------------------------------|----------|---------------------------------|
| Pure lactose .....                                                                   | 8.8 c.c. | } = 50 c.c. Pavy's<br>solution. |
| Lactose and pancreatic juice of<br>dog injected with extract of<br>kitten's gut..... | 8.0 „    |                                 |
| Inversion of 22 per cent. of the lactose.                                            |          |                                 |

A modification of this method was subcutaneously to inject into biscuit-fed dogs a  $\text{CHCl}_3$  water extract of intestinal mucous membrane of kittens or of milk-fed dogs. Two injections were made on successive days, and on the third day the pancreatic juice was collected and examined. In all these cases lactase was produced, as shown by the following table:—

TABLE II.—Figures representing the number of c.c. which reduced 50 c.c. Pavy's solution.

| Experiment. | Pure Lactose. | Lactose + Juice. | Degree of Inversion. |
|-------------|---------------|------------------|----------------------|
|             | C.c.          | C.c.             | Per cent.            |
| I .....     | 7.4           | 6.8              | 19                   |
| II .....    | 7.8           | 7.5              | 9.3                  |
| III .....   | 7.05          | 6.75             | 10                   |
| IV .....    | 7.95          | 7.65*            | 9                    |
| V .....     | 8.8           | 8.0              | 22                   |

\* Control, 8.0 c.c.

As far as they go, these experiments show that the intestinal mucous membrane of milk-fed animals, injected into dogs not fed on milk, causes the pancreas to secrete lactase, whereas lactose or extracts of mucous membrane injected separately have no such action. In the present stage of this investigation no complete explanation of these results can be offered. But it seems probable that as a result of the action of the intestinal mucous membrane on lactose, some chemical substance is formed, which passes by the blood-stream to the pancreas, where it stimulates the latter to manufacture a specific enzyme—lactase.

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"On the Bending of Waves round a Spherical Obstacle."

LORD RAYLEIGH, F.R.S. Received May 1,—Read May 1903.

In the 'Proceedings' for January 21, 1903, Mr. H. M. Macdonald discusses the effect of a reflecting spherical obstacle upon electrical aerial waves for the case where the radius of the sphere is  $l$  compared with the wave-length ( $\lambda$ ) of the vibrations. The remarkable success of Marconi in signalling across the Atlantic suggests a more decided bending or diffraction of the waves round the protuberance of the earth than had been expected, and it imparts a great interest to the theoretical problem. Mr. Macdonald's results, if they can be accepted, certainly explain Marconi's success; but they appear to me to be open to objection.

If  $C$  be the source of sound,  $P$  a point upon the sphere whose centre is at  $O$ ,  $\phi_1$  the velocity-potential at  $P$  due to the source (in the absence of the sphere),  $\chi$  the angle subtended by  $OC$ , Mr. Macdonald finds the actual potential at  $P$ ,

$$\phi = \phi_1 (1 - \cos \chi) \dots\dots\dots$$

so that there is no true shadow near the surface of the sphere. If  $C$  be infinitely distant, and  $\mu$  denote (as usual) the cosine of the angle between  $OP$  and  $OC$ ,

$$\phi = \phi_1 (1 + \mu) \dots\dots\dots$$

That the sound should vanish at the point opposite, and be quadrupled at the point immediately under the source is what would be expected; but that (however large the sphere) the shadow should be so imperfect, for example,  $\mu = -\frac{1}{2}$ , is indeed startling.

The first objection that I have to offer is that nothing of this kind is observed in the case of light. The relation of wave-length to diameter of obstacle is about the same in Marconi's phenomenon as when visible light impinges upon a sphere 1 inch (2.54 cm.) in diameter. So far as I am aware no creeping of light into the dark hemisphere through any sensible angle is observed under these conditions even though the sphere is highly polished.\*

But I shall doubtless be asked whether I have any complaint against the mathematical argument which leads up to (2).

As in *Theory of Sound*, § 334, the question relates to the ratio between a certain function of  $c$  (the radius) and its differential

\* It may be remarked that at the centre of the shadow thrown at some distance (say 1 metre) behind, there is a bright spot similar to that seen when a disc is substituted for the sphere. This effect is observed with a magnifying lens. If the eye, situated at the centre of the shadow, be focused upon the sphere, the edge of the obstacle is seen bounded by a very narrow ring of light.

coefficient with respect to  $c$ . The function is that which occurs in the representation of a disturbance which travels outwards, and (§ 323) may be denoted by

$$\frac{e^{-i\kappa c}}{c} f_n(i\kappa c) \dots\dots\dots (3),$$

where

$$\kappa = 2\pi/\lambda,$$

and

$$f_n(i\kappa c) = 1 + \frac{n(n+1)}{2 \cdot i\kappa c} + \frac{(n-1) \dots (n+2)}{2 \cdot 4 \cdot (i\kappa c)^2} + \dots\dots\dots (4).$$

The differential coefficient of (3) is

$$-\frac{e^{-i\kappa c}}{c^2} \{ (1 + i\kappa c) f_n(i\kappa c) - i\kappa c f'_n(i\kappa c) \} \dots\dots\dots (5),$$

so that the ratio in question takes the form

$$\frac{-c f_n(i\kappa c)}{(1 + i\kappa c) f_n(i\kappa c) - i\kappa c f'_n(i\kappa c)} \dots\dots\dots (6).$$

In these expressions  $n$  is the order of the Legendre's function  $P_n(\mu)$  which occurs in the series representative of the velocity-potential.

When  $\kappa c$  is very great, the ratio expressed in (6) may assume a simplified form. From (4) we see that, if  $n$  be finite,

$$f_n(i\kappa c) = 1, \quad i\kappa c f'_n(i\kappa c) = 0,$$

ultimately, so that

$$(6) = -\frac{1}{i\kappa}, \quad \dots\dots\dots (7),$$

independent of  $n$ .

This is the foundation of the simple result reached by Mr. Macdonald. Its validity depends, therefore, upon the applicability of (7) to all values of  $n$  that need to be regarded. If when  $\kappa c$  is infinite, only finite values of  $n$  are important, (7) is sufficiently established; but (§ 328) it appears that under these conditions the most important terms are of infinite order. I think it will be found that for the most important terms  $n$  is approximately equal to  $\kappa c$ , and that accordingly (7) is not available. In any case it could not be relied upon without a further examination.

In *Theory of Sound*, § 328, the problem is treated for the case where  $\kappa c$  is small, and the calculation is pushed as far as  $\kappa c = 2$ . The results indicate no definite shadow. I have commenced a calculation for  $\kappa c = 10$ , about the highest value for which the method is practicable. But it is doubtful whether even this value is high enough to throw light upon what happens when  $\kappa c$  is really large.

“Sur la Diffraction des Ondes Electriques : à propos d'un Article de M. Macdonald.” Par H. POINCARÉ, For. Mem. R.S. Received May 4,—Read May 28, 1903.

1. Dans le No. 472 des Proceedings, M. Macdonald a publié un article intitulé : “The Bending of Electric Waves round a Conducting Obstacle,” sur lequel je désire présenter quelques observations. On a annoncé récemment que M. Marconi avait réussi à envoyer des signaux de télégraphie sans fil d'Angleterre en Amérique. Quelle que soit la sensibilité du cohéreur, ce résultat est bien fait pour nous surprendre pour deux raisons : à cause de la grande distance d'abord, et à cause de la courbure de la Terre. Evidemment il faut admettre qu'une grande partie de la radiation a subi une diffraction considérable, pour pouvoir contourner l'obstacle formé par la Terre.

L'importance de cette diffraction est-elle uniquement due à la grande longueur des ondes ? M. Macdonald ne l'a pas pensé. Nous savons que M. Gouy a observé des phénomènes, qu'il appelle de diffraction éloignée, en concentrant de la lumière sur le tranchant d'un rasoir. Les rayons lumineux subissent ainsi des déviations considérables. J'ai fait dans les ‘Acta Mathematica’ la théorie de ces phénomènes, et j'ai montré qu'ils sont indépendants de la longueur d'onde, pourvu que le rayon de courbure du tranchant et la distance de ce tranchant au foyer où se concentre la lumière restent du même ordre de grandeur que cette longueur d'onde.

D'après M. Macdonald, il se passerait quelque chose d'analogue en télégraphie sans fil ; l'onde émanée d'un excitateur dont la distance au sol est de l'ordre de la longueur d'onde, suivrait la surface de la sphère terrestre sans s'affaiblir sensiblement. Il y a là une idée qui au premier abord est assez séduisante ; mais si on examine de plus près l'analyse de M. Macdonald on voit qu'il n'a pas supposé que la source de lumière soit à une distance du sol comparable à la longueur d'onde. Ses formules restent, ou semblent rester, applicables quelle que soit cette distance. Si alors la lumière reste sensible quelle que soit la longueur d'onde et quelle que soit la position de la source, cela veut dire qu'il fait jour pendant toute la nuit ; cette conclusion est trop manifestement contredite par l'expérience.

Il est vrai que M. Macdonald suppose que le point d'où l'on observe la lumière est situé sur la surface même de la sphère terrestre ; on pourrait imaginer alors qu'il y a une couche très mince, d'épaisseur comparable à la longueur d'onde où la lumière est sensible, et qu'en dehors de cette couche elle est insensible. Mais en regardant de plus près, on voit que l'analyse de M. Macdonald s'applique tout aussi bien si on observe d'un point quelconque de l'espace. Il y a donc dans cette

analyse un point faible, et il importe de le découvrir afin de voir ce qui reste de ses conclusions.

2. Rappelons le principe de l'analyse de M. Macdonald. Introduisons les fonctions de Bessel :

$$J_n(x) = A_n x^n \int_{-i}^{+i} e^{zx} (z^2 + 1)^{\frac{2n-1}{2}} dz \dots\dots\dots (1).$$

$$\text{et} \quad I_n(x) = A'_n x^n \int_{-i}^{\infty} e^{zx} (z^2 + 1)^{\frac{2n-1}{2}} \dots\dots\dots (2).$$

Toutes deux satisfont à l'équation différentielle

$$J'' + \frac{J'}{x} + \left(1 - \frac{n^2}{x^2}\right) J = 0 \dots\dots\dots (3).$$

La première est caractérisée par ce fait qu'elle reste finie dans toute l'étendue du plan, et la seconde parce que pour  $x$  très grand elle est sensiblement proportionnelle à

$$\frac{e^{ix}}{\sqrt{x}}.$$

Elle ne diffère que par un facteur constant de celle que M. Macdonald appelle  $K_n$ . Quant à  $A_n$  et  $A'_n$  ce sont des coefficients constants sur lesquels nous reviendrons.

Revenons au problème qui nous occupe. Prenons pour axe des  $z$  la droite qui joint le centre de la Terre à l'excitateur ; appelons  $r$  la distance du point considéré au centre de la Terre, et  $\rho$  la distance à l'axe des  $z$ . Prenons pour unité le rayon de la Terre de telle sorte que  $r = 1$  soit l'équation de la surface de la Terre. Posons enfin  $z = r\mu$ .

Soit  $2\pi/k$  la longueur d'onde, les forces électriques ou magnétiques dépendront des lignes trigonométriques de l'angle  $kVt$ , si  $V$  est la vitesse de la lumière ; et je pourrai, par un artifice bien connu, supposer que chacune de ces forces est la partie réelle d'une expression imaginaire proportionnelle à  $e^{-ikVt}$ . Supposons donc que la force magnétique soit la partie réelle de

$$\frac{\psi}{\rho} e^{-itVt},$$

où  $\psi$  est une expression imaginaire indépendante du temps. M. Macdonald indique d'abord quelle est la forme générale de l'expression  $\psi$ , il trouve :

$$\psi = \sqrt{r} \Sigma [B_n J_{n+\frac{1}{2}}(kr) + C_n I_{n+\frac{1}{2}}(kr)] (1 - \mu^2) \frac{dP_n}{d\mu} \dots\dots (4),$$

$P_n$  désignant le polynôme de Legendre.

C'est là la solution la plus générale de l'équation :

$$\frac{d^2\psi}{d\rho^2} + \frac{1 - \mu^2}{r^2} \frac{d^2\psi}{d\mu^2} + k^2\psi = 0 \dots\dots\dots (5),$$

à laquelle doit satisfaire  $\psi$  (en dehors des sources) toutes les fois que sources sont distribuées de telle façon que tout soit de révolution autour de l'axe des  $z$ . Si nous considérons une sphère de rayon  $a$ , si en dehors de cette sphère il n'y a pas de source, alors à l'extérieur cette sphère, la fonction  $\psi$  devra être représentée par une expression la forme (4); de plus, pour  $r$  très grand, nous devons avoir des termes contenant en facteurs l'exponentielle :

$$e^{ik(r-Vt)},$$

et qui correspondent à des faisceaux divergents s'éloignant des sources, et ne pas avoir de termes contenant en facteurs l'exponentielle  $e^{-ik(r+Vt)}$  et qui correspondraient à des faisceaux convergeant vers sources. Il en résulte que les coefficients  $B_n$  sont nuls.

Supposons au contraire qu'il n'y ait à l'intérieur de la sphère de rayon  $a$  ni source ni surface réfléchissante comme serait à la surface de Terre dans le problème qui nous occupe. Alors à l'intérieur de cette sphère la fonction  $\psi$  sera encore représentée par une expression de forme (4), mais comme cette fonction doit demeurer finie pour  $r=0$  sont les coefficients  $C_n$  qui seront nuls.

Dans le problème qui nous occupe nous poserons :

$$\psi = \psi_1 + \psi_2,$$

où  $\psi_1$ , sera ce que serait la fonction  $\psi$  avec la même source, si la surface réfléchissante de la Terre était supprimée. On aura alors :

$$\psi_1 = \rho \frac{d}{d\rho} \frac{e^{ikR}}{R},$$

$R$  étant la distance du point considéré à la source ; soit  $a$  la distance de cette source au centre de la Terre, à l'extérieur de la sphère de rayon  $a$  on aura

$$\psi_1 = \sqrt{r} \Sigma C_n I_{n+\frac{1}{2}} Q_n, \dots\dots\dots (4 b)$$

et à l'intérieur

$$\psi_1 = \sqrt{r} \Sigma B_n J_{n+\frac{1}{2}} Q_n. \dots\dots\dots (4 c)$$

$C_n$  et  $B_n$  sont des coefficients constants, et j'ai posé pour abrégé :

$$Q_n = (1 - \mu^2) \frac{dP_n}{d\mu}.$$

D'autre part, à l'extérieur de la sphère de rayon 1 on devra avoir :

$$\psi_2 = \sqrt{r} \Sigma C_n'' I_{n+\frac{1}{2}} Q_n.$$

On déterminera les coefficients constants  $C_n''$  par la condition :

$$\frac{d\psi}{dr} = 0,$$

qui doit être satisfaite pour  $r = 1$ . On trouve ainsi :

$$0 = \frac{d\psi_1}{dr} + \frac{d\psi_2}{dr} = \sqrt{r} \Sigma B'_n \frac{dJ_{n+\frac{1}{2}}}{dr} Q_n + \Sigma C''_n \frac{dI_{n+\frac{1}{2}}}{dr} Q_n \\ + \frac{1}{2\sqrt{r}} \Sigma (B'_n I_{n+\frac{1}{2}} + C''_n I_{n+\frac{1}{2}}) Q_n \dots\dots (6),$$

d'où la condition

$$\left( B'_n \frac{dJ_{n+\frac{1}{2}}}{dr} + C''_n \frac{dI_{n+\frac{1}{2}}}{dr} \right) + \frac{1}{2r} (B'_n J_{n+\frac{1}{2}} + C''_n I_{n+\frac{1}{2}}) = 0 \dots (7),$$

qui doit être satisfaite pour  $r = 1$  et qui détermine  $C''_n$ .

Mais si la longueur d'onde est très petite,  $k$  est très grand et  $I_{n+\frac{1}{2}}$  est sensiblement égal à :

$$A \frac{e^{ikr}}{\sqrt{kr}}.$$

$A$  étant une constante, sa dérivée par rapport à  $r$  est sensiblement

$$ikA \frac{e^{ikr}}{\sqrt{kr}},$$

de sorte que l'on a sensiblement

$$\frac{dI_{n+\frac{1}{2}}}{dr} = ikI_{n+\frac{1}{2}},$$

et par conséquent,

$$\frac{d\psi_2}{dr} = ik\psi_2 + \frac{1}{2r} \psi_2 \dots\dots\dots (8),$$

ou encore comme  $k$  est très grand par rapport à  $1/r$

$$\frac{d\psi_2}{dr} = ik\psi_2 \dots\dots\dots (8 \text{ bis}).$$

La condition (6) devient donc

$$\frac{d\psi_1}{dr} + ik\psi_2 = 0$$

de sorte qu'on a pour  $r = 1$ ,

$$\psi = \psi_1 + \psi_2 = \psi_1 + i \frac{d\psi_1}{kdr}.$$

Il est aisé de constater que cette expression ne s'annule pas, et même n'est pas très petite, de sorte que sur la surface même de la sphère terrestre il devrait rester de la lumière.

Si nous supposons maintenant  $r > 1$  ; et si nous appelons  $I'_{n+\frac{1}{2}}$ ,  $\psi'_2$ ,  $\psi'_1$ ,  $\frac{d\psi'_2}{dr}$ ,  $\frac{d\psi'_1}{dr}$  les valeurs de  $I_{n+\frac{1}{2}}$ ,  $\psi_2$ ,  $\psi_1$ ,  $\frac{d\psi_2}{dr}$ ,  $\frac{d\psi_1}{dr}$  pour  $r = 1$ , nous aurons :—

$$I_{n+\frac{1}{2}} = I_{n+\frac{1}{2}}^{\circ} \frac{e^{ikr}}{\sqrt{r}}; \quad \psi_2 = \psi_2^{\circ} e^{ikr} = i \frac{d\psi_1^{\circ}}{dr} \frac{e^{ikr}}{k};$$

et on aurait

$$\psi = \psi_1 + \psi_2 = \psi_1 + i \frac{d\psi_1^{\circ}}{kdr} e^{ikr}.$$

Ainsi il devrait y avoir encore de la lumière, même à l'extérieur d sphère terrestre ; c'est ce que j'avais annoncé plus haut.

3. Ce résultat étant manifestement erroné, il faut chercher quel le point faible de l'analyse précédente. C'est évidemment la façon d nous avons établi les égalités (8) et (8 bis). Nous avons :

$$\frac{d\psi_2}{dr} - ik\psi_2 - \frac{1}{2r} \psi_2 = \sqrt{r} \Sigma C'_n \left( \frac{dI_{n+\frac{1}{2}}}{dr} - ikI_{n+\frac{1}{2}} \right) Q_n \dots$$

Le second membre de (9) est une série dont tous les termes tend vers zéro quand  $k$  croît indéfiniment. Nous en avons conclu la somme de la série tendait aussi vers zéro, et que par conséquent le premier membre de (9) était sensiblement nul pour  $k$  très grand, qui nous donnait l'égalité (8). *Mais cette conclusion ne serait légitime que si la série était uniformément convergente, j'entends uniformément rapport à  $k$ .*

Or, la condition n'est pas remplie pour notre série, et il est aisé constater d'abord qu'elle ne l'est pas pour la série analogue

$$\sqrt{r} \Sigma C'_n \left( \frac{dI_{n+\frac{1}{2}}}{dr} - ikI_{n+\frac{1}{2}} \right) Q_n$$

formée à l'aide de la série (4 bis). Si elle l'était en effet, on aurait :

$$\frac{d\psi_1}{dr} - ik\psi_1 - \frac{1}{2r} \psi_1 = 0 \dots\dots\dots (1)$$

et comme l'expression de  $\psi_1$  est connue et très simple, on voit médiatement qu'il n'en est pas ainsi. Cette relation (10) si elle est exacte, entraînerait comme conséquence que

$$\psi_1 = \rho \frac{d}{d\rho} \frac{e^{ikR}}{R}$$

serait le produit d'une fonction de  $r$  par une fonction de  $\mu$ , ce manifestement n'est pas vrai.

4. Ce qui précède se rattache immédiatement à l'étude des potentiels généralisés. Je désigne ainsi les intégrales de la forme

$$W = \int h \frac{e^{ikR}}{R} d\sigma,$$

où l'intégration doit être étendue à tous les éléments  $d\sigma$  d'une surface ou d'un volume attirant ; où  $h$  est une fonction des coordonnées

l'élément  $d\sigma$ , représentant la densité de la matière attirante; où enfin  $R$  désigne la distance de cet élément  $d\sigma$  au point de coordonnées courantes.

On aura d'ailleurs pour  $W$  une formule analogue à (4)

$$W = \Sigma [E_n J_{n+\frac{1}{2}}(kr) + F_n I_{n+\frac{1}{2}}(kr)] P_n, \dots\dots\dots (11),$$

où  $P_n$  est une fonction sphérique d'ordre  $n$ , qui se réduit au polynôme de Legendre, si comme nous le supposons ici tout est de révolution autour de l'axe des  $z$ .

Soient

$$x' = r' \sqrt{1 - \mu'^2} \cos \theta' \quad y' = r' \sqrt{1 - \mu'^2} \sin \theta', \quad z' = r' \mu',$$

les coordonnées de l'élément  $d\sigma$ ; si tout est de révolution autour de l'axe des  $z$  comme nous le supposons,  $h$  ne dépendra que de  $r'$  et de  $\mu'$ . On aura d'ailleurs :

$$\psi = \rho \frac{dW}{d\rho}.$$

Si toutes les masses attirantes sont à l'intérieur de la sphère de rayon  $a$ , on aura à l'extérieur de cette sphère:  $E_x = 0$ ; et d'un raisonnement tout pareil à celui qui précède, il semblera résulter que l'on doit avoir :

$$\frac{dW}{dr} = ikW.$$

Seulement ici, il sera plus aisé de voir dans quels cas ce raisonnement est légitime.

Commençons par étudier le cas d'un potentiel de simple couche répandu à la surface d'une sphère de rayon 1; nous devons donc supposer que l'on a

$$r = 1, \quad d\sigma = d\mu' d\theta',$$

et que  $h$  est fonction de  $\mu'$  seulement.

Nous examinerons seulement deux cas : 1° celui où  $h$  est une fonction continue indépendante de  $k$ ; 2° celui où l'on a :

$$h = e^{ikZ} h_0,$$

$Z$  et  $h_0$  étant des fonctions continues indépendantes de  $k$ .

Dans le premier cas, la densité de la matière attirante ne varie que lentement sur la surface de la sphère; dans le second cas, au contraire, elle varie très rapidement, et d'autant plus rapidement que  $k$  est plus grand. On aura alors :

$$W = \int e^{ik(R+Z)} \frac{h_0}{R} d\mu' d\theta'.$$

Dans le premier cas,  $Z$  se réduit à zéro et  $h_0$  à  $h$ .



Pour aller plus loin, envisageons d'abord l'intégrale simple :

$$\int_a^b e^{ik\phi(z)} \psi(z) dz,$$

où  $\phi$  et  $\psi$  sont des fonctions de  $z$  que nous supposons holomorphes indépendantes de  $k$  dans la région envisagée. Nous supposons que  $a$  et  $b$  sont réels, que l'intégration se fait le long d'un chemin réel, que pour  $z$  réel les fonctions  $\phi$  et  $\psi$  sont réels.

Nous allons déformer ce chemin d'intégration de façon que le long du nouveau chemin la partie imaginaire de  $\phi(z)$  soit positive sauf certains points exceptionnels pour lesquels elle sera nulle.

Il est toujours possible de déformer le chemin de cette manière, et seuls points exceptionnels qu'on est obligé de laisser subsister, et pour lesquels la partie imaginaire de  $\phi(z)$  doit rester nulle, ce sont les extrémités du chemin  $a$  et  $b$ , et d'autre part les points où le chemin doit traverser l'axe des  $z$  réels, parce que la région où la partie imaginaire de  $\phi(z)$  est positive, passe d'un côté à l'autre de cet axe des  $z$  réels ; ces points sont ceux pour lesquels la dérivée  $\phi'(z)$  est nulle. Par exemple si on suppose  $\phi(z) = z^2$  ; et  $z = x + iy$  ; la région où la partie imaginaire est positive est donnée par l'inégalité  $yx > 0$  ; donc pour  $x < 0$ , on doit avoir  $y < 0$ , et pour  $x > 0$  on doit avoir  $y > 0$  ; donc quand  $x$  passe par la valeur zéro, notre région passe d'un côté à l'autre de l'axe des  $z$  ; si donc nous voulons que notre chemin d'intégration reste constamment dans cette région, nous pouvons éviter de le faire passer par l'origine.

Toutes les fois que la partie imaginaire de  $\phi(z)$  est positive, l'exponentielle  $e^{ik\phi(z)}$  tend rapidement vers 0 quand on fait croître  $k$ . Si donc  $k$  est très grand, on aura une valeur très approchée de l'intégrale, en réduisant le chemin d'intégration aux parties très voisines des points exceptionnels. Soit donc  $a$  l'un des points exceptionnels autres que  $a$  et  $b$  ; notre intégrale se réduira à fort près à :

$$\int_a^{a+\epsilon} + \sum \int_{a-\epsilon}^{a+\epsilon} + \int_{b-\epsilon}^b.$$

Nous sommes donc ramenés au calcul d'intégrales de la forme :

$$K = \int_a^{a+\epsilon} e^{ik\phi(z)} \psi(z) dz, \quad K' = \int_{a-\epsilon}^a e^{ik\phi(z)} \psi(z) dz.$$

Soit alors  $H + A(z - \alpha)^m$ ,  $B(z - \alpha)^p$  les premiers termes du développement de  $\phi$  et de  $\psi$  suivant les puissances de  $z - \alpha$  ; on aura toujours avec la même approximation :

$$K = e^{ikH} \int_0^\infty B e^{ikA z^m} z^p dz, \quad K' = e^{ikH} \int_{-\infty}^0 B e^{ikA z^m} z^p dz.$$

On doit dans ces intégrales faire tendre  $z$  vers l'infini (limite supérieure ou inférieure d'intégration) avec un argument tel que  $e^{ikz}$  tende vers zéro. Ces intégrales sont des fonctions eulériennes faciles à calculer.

Si maintenant les fonctions  $\phi(z)$  et  $\psi(z)$  sont périodiques de période  $b-a$ , nous pouvons supprimer les termes correspondant aux deux extrémités  $a$  et  $b$  et ne plus considérer ces points  $a$  et  $b$  comme exceptionnels. On a en effet

$$\int_a^b = \int_{a+h}^{b+h},$$

et nous pouvons donner à  $h$  une valeur imaginaire telle que  $\phi(a+h) = \phi(b+h)$  ait sa partie imaginaire positive.

Les seules parties du chemin d'intégration qu'il y a lieu de conserver sont celles qui avoisinent les points où  $\phi'(z)$  est nul.

Les mêmes considérations peuvent s'appliquer aux intégrales doubles de la forme :

$$\iint e^{ik\phi(x,y)} \psi(x,y) dx dy$$

étendues à une aire plane  $S$  limitée par une ligne fermée  $L$ . On verrait sans peine (soit en intégrant d'abord, par rapport à  $y$ , puis par rapport à  $x$ , et appliquant chaque fois les principes que nous venons d'établir, soit en s'appuyant sur les propriétés des intégrales doubles imaginaires), comme nous venons de le faire sur celles des intégrales simples imaginaires, on verrait, dis-je, que l'on peut réduire l'aire d'intégration tout entière aux parties voisines de la ligne  $L$ , et aux parties voisines des maxima, minima et minimax de la fonction  $\phi(x, y)$ , et dont le calcul pourrait se faire aisément.

Il en serait de même pour l'intégrale

$$\int e^{ik\phi} \psi d\sigma,$$

étendue à tous les éléments  $d\sigma$  d'une aire courbe  $S$  limitée par une ligne fermée  $L$ , et située sur une surface fermée  $\Sigma$ . Quant à  $\phi$  et  $\psi$ , ce sont bien entendu des fonctions analytiques des coordonnées de l'élément  $d\sigma$ .

Si nous supposons que l'intégration soit étendue à la surface fermée tout entière, et qu'il n'y ait plus de ligne  $L$ , il suffira de réduire la surface d'intégration aux parties voisines des maxima, minima ou minimax de la fonction  $\phi$ .

Revenons au problème qui nous occupe, et commençons par le premier cas, celui où

$$W = \int e^{ikR} \frac{h}{R} d\sigma,$$

$h$  étant indépendant de  $k$ ; il suffira alors de réduire le ~~cha~~  
d'intégration aux parties voisines des maxima de  $R$ . Soit  $M$  le po~~nt~~  
de coordonnées courantes,  $P$  le centre de gravité de l'élément  $d\sigma$ ;  
n'est autre chose que la distance  $MP$ . Le maximum et le minim~~um~~  
de la distance  $MP = R$  correspondant aux deux intersections de ~~la~~  
sphère avec la droite  $MO$  qui joint le point  $M$  au centre de la sph~~ère~~  
leur valeur est  $r+1$  et  $r-1$ . Soit alors  $P_0$  et  $P_1$  les deux po~~ints~~  
d'intersection de la sphère avec  $MO$ ; pour un point  $P$  voisin de  $P_0$  on  
aura sensiblement  $MP^2 = (r+1)^2 + PP_0^2$  et pour un point voisin de  $P_1$   
ou aura  $MP^2 = (r-1)^2 + PP_1^2$  d'où :

$$R = (r+1) + \frac{PP_0^2}{2(r-1)}, \quad R = (r-1) + \frac{PP_1^2}{2(r-1)}.$$

On voit alors que l'intégrale  $W$  peut se réduire aux parties pro-  
venant du voisinage des points  $P_0$  et  $P_1$ ; le voisinage de  $P_0$  nous donne  
sensiblement un terme de la forme :

$$\frac{e^{ik(r+1)}}{k} f,$$

et le voisinage de  $P_1$  un terme de la forme

$$\frac{e^{ik(r-1)}}{k} f_1,$$

$f$  et  $f_1$  étant indépendants de  $k$ . Nous aurons donc sensiblement

$$W = \frac{e^{ik(r+1)} f + e^{ik(r-1)} f_1}{k}.$$

Le terme le plus important de  $dW/dr$ , celui devant lequel les autres  
doivent être négligés, est alors :

$$\frac{dW}{dr} = i [e^{ik(r+1)} f + e^{ik(r-1)} f_1].$$

On a donc

$$\frac{dW}{dr} = ikW,$$

ce qui est bien le résultat auquel aurait conduit le raisonnement de  
M. Macdonald.

Mais passons maintenant au second cas, et pour préciser davantage,  
soit  $Q$  un point fixe extérieur à la sphère et que nous appellerons la  
source; nous supposons que  $Z$  n'est autre chose que la distance  $PQ$ .

Voici ce qui justifie ce choix. Nous avons vu plus haut que  $\psi_2$   
devait être défini par la condition

$$\frac{d\psi_2}{dr} = -\frac{d\psi_1}{dr}.$$

qui doit être satisfaite pour  $r = 1$ . Or, précisément  $\frac{d\psi_1}{dr}$  pour  $r = 1$  est de la forme

$$e^{ikPQ}h_0,$$

le point Q étant l'excitateur, et  $h_0$  restant fini pour  $k$  très grand. L'analogie des deux problèmes est ainsi mise en évidence.

Soit donc :

$$W = \int e^{ik(R+Z)} \frac{h_0}{R} d\sigma.$$

On pourra réduire la surface d'intégration aux parties de la sphère voisines des maxima, minima et minimax de

$$R + Z = MP + PQ.$$

Les minima de  $MP + PQ$  correspondront évidemment aux points P qui sont en ligne droite avec M et Q, c'est à dire, aux deux points d'intersection  $P_0$  et  $P_1$  de la sphère avec la droite MQ.

On obtiendra encore des maxima et des minimax en construisant des ellipsoïdes de révolution ayant M et Q pour foyers et tangents à la sphère. Si les deux points M et Q sont voisins de la sphère, on obtiendra ainsi deux points réels  $P_2$  et  $P_3$ . Alors notre champ étant réduit au voisinage des points  $P_0, P_1, P_2, P_3$ , et comme d'ailleurs

$$MP_0 + P_0Q = MP_1 + P_1Q = MQ,$$

on aura sensiblement, par un calcul tout pareil à ceux qui précèdent :

$$W = \frac{1}{k} [e^{ikMQ}f_1 + e^{ik(MP_1+P_1Q)}f_2 + e^{ik(MP_3+P_3Q)}f_3],$$

$f_1, f_2$ , et  $f_3$  restant finis pour  $k$  infini, et on en déduit

$$\frac{dW}{dr} = i [e^{ikMQ}f_1 \cos \alpha_1 + e^{ik(MP_1+P_1Q)}f_2 \cos \alpha_2 + e^{ik(MP_3+P_3Q)}f_3 \cos \alpha_3],$$

où  $\alpha_1, \alpha_2$  et  $\alpha_3$  désignent les angles que font les trois droites MQ,  $MP_2$  et  $MP_3$  avec le rayon vecteur MO. On voit ainsi que la condition

$$\frac{dW}{dr} = ikW,$$

à laquelle conduirait le raisonnement de M. Macdonald n'est pas remplie.

Il est donc certain dans ce cas que la convergence des séries procédant suivant les fonctions de Bessel n'est pas uniforme.

Ces considérations suffiront, je pense, pour faire comprendre le point faible du raisonnement de M. Macdonald; il serait important de reprendre les calculs en tenant compte de cette difficulté, car il y a lieu de se demander si les résultats obtenus par M. Marconi peuvent

s'expliquer par les théories actuelles, et sont dus simplement à l'exquise sensibilité du cohéreur, ou s'ils ne prouvent pas que les ondes se réfléchissent sur les couches supérieures de l'atmosphère rendues conductrices par leur extrême raréfaction.

"The Measurement of Tissue Fluid in Man. Preliminary Note."

By GEORGE OLIVER, M.D., F.R.C.P. Communicated by Sir LAUDER BRUNTON, F.R.S. Received in revised form May 18, —Read June 11, 1903.

The object of this preliminary note is to indicate a method by which the tissue fluid in man may be measured, thus enabling the observer to ascertain the conditions under which it is effused and disposed of.

In the course of some observations made with the view of eliminating tissue fluid as a cause of variability in the samples of blood obtained for examination, I found that the rolling of a tight rubber ring over the finger from the tip to beyond the interphalangeal joints will, as a rule, considerably raise the percentages of the blood corpuscles, and of the hæmoglobin. I could not arrive at any other conclusion, than that the ring not merely empties the vessels, but likewise clears away any tissue fluid present in the skin and subcutaneous tissues. The needle, in puncturing the capillaries, liberates a certain portion of lymph from the areolar tissue which surrounds them, and this dilutes the blood. When, however, both fluids have been dispersed as much as possible by the compression of the firm rubber ring, a puncture made just before removing the ring yields blood *per se*; for the blood instantly returns to the vessels, whereas an appreciable interval must elapse before the lymph reappears, or is exuded afresh. I, therefore, inferred that the reading of the difference in the percentage of the corpuscles, or of the hæmoglobin, before and after the use of the ring, provides a measure of the tissue-lymph, and makes the study of the circulation of it in man possible.

This simple method having furnished somewhat unexpected results, I naturally accepted them at first with reserve; and, for some time, the data were allowed to accumulate, until at last it was quite apparent that they invariably fell into the same order. Inasmuch as the method did not provide results which were exceptional or erratic, or contradictory and unaccountable, reliability on it became gradually established by the mere repetition of the observations.

A number of observations have been made on normal subjects leading a quiescent life, with comparative rest of the muscles; and on persons subjected to varying degrees of exercise, and to different

peratures and altitudes. In this note I limit myself, however, to a statement of results obtained in the former class of subjects only.

On the numerous observations which this inquiry necessitated on the muscles, and on the hæmoglobin, were made by the hæmocytometer, and the hæmoglobinometer, which were described by me before the Physiological Society some few years ago,\* and the specific gravity of the blood was determined by Roy's method. The blood-pressures (arterial, capillary, and venous) were read by the hæmodynamometer,†

Hill and Barnard's sphygmometer, and Professor Gärtner's meter, were also occasionally used in determining the arterial pressure.

Some of the general conclusions afforded by the observations may be epitomised:—

The amount of tissue fluid varies at different times in the course of the day; and each variation is of short duration.

The ingestion of food produces a rapid flow of lymph into the tissue spaces, which in an hour after the meals acquires its maximum development, and then it slowly subsides, and only ceases to be apparent after the lapse of from 3—4 hours.

The digestive curve of variation always follows the same general type; the rise being rapid, the acme short, and the subsidence gradual. The variations were observed to follow this well-defined order in all the healthy subjects so far submitted to observation. The curve of variation is, therefore, rhythmical—the wave abruptly rising to an acme, and then somewhat slowly subsiding.

The following are two examples:—

*Example 1.*

|                       | Corpuscles per cent.      |   | Diff.   | Percentage of lymph. |
|-----------------------|---------------------------|---|---------|----------------------|
| Before the meal       | 99‡ (4,950,000 per c.mm.) | } | 200,000 | 4                    |
| Breakfast)            | 103 (5,150,000 „ )        |   |         |                      |
| One hour after ...    | 91 (4,550,000 „ )         | } | 750,000 | 15                   |
|                       | 106 (5,300,000 „ )        |   |         |                      |
| Two hours after ...   | 94 (4,700,000 „ )         | } | 550,000 | 11                   |
|                       | 105 (5,250,000 „ )        |   |         |                      |
| Three hours after ... | 96 (4,800,000 „ )         | } | 400,000 | 8                    |
|                       | 104 (5,200,000 „ )        |   |         |                      |
| Four hours after ...  | 98 (4,900,000 „ )         | } | 150,000 | 3                    |
|                       | 101 (5,050,000 „ )        |   |         |                      |

See 'Journal of Physiology,' Cambridge and London, vol. 19, p. xv.

*Ibid.*, vols. 22, 23.

The figure on the first line represents the percentage of corpuscles before, and the figure on the second line that after, compression of the finger by the rubber

*Example 2.*

|                   | Corpuscles per cent.     |   | Diff.   | Percentage of lymph |
|-------------------|--------------------------|---|---------|---------------------|
| Before the meal   | 99 (4,950,000 per c.mm.) | } | None    | 0                   |
| (dinner)          | 99 (4,950,000 "          |   |         |                     |
| 1 hour after ...  | 91 (4,550,000 "          | } | 850,000 | 17                  |
|                   | 108 (5,400,000 "         |   |         |                     |
| 2 hours after ... | 94 (4,700,000 "          | } | 600,000 | 12                  |
|                   | 106 (5,300,000 "         |   |         |                     |
| 3 hours after ... | 104 (5,200,000 "         | } | None    | 0                   |
|                   | 104 (5,200,000 "         |   |         |                     |

4. The amount of lymph is proportionate to the rise of the n arterial and capillary pressures, and these pressures have l found to follow exactly the same prolonged rhythmical co after the ingestion of food, as does the effusion of lymph.

The following example shows the agreement between the bl pressures and the amount of lymph :—

|                                  | Percentage of lymph. | Mean arterial pressure. |
|----------------------------------|----------------------|-------------------------|
| Before the meal .....            | None                 | 100 c.mm. Hg.           |
| $\frac{1}{2}$ hour after .....   | 10                   | 110 "                   |
| 1 hour after .....               | 16                   | 116 "                   |
| $1\frac{1}{2}$ hours after ..... | 8                    | 108 "                   |
| 2 hours after.....               | 5                    | 105 "                   |
| 3 hours after.....               | None                 | 100 "                   |

The method devised for observing the capillary pressure is not q so delicate for the smaller variations as I could wish, and I am ho to improve it ; but it is sufficiently definite to show that the capil blood-pressure is raised throughout the digestive circulatory disturbs and especially so at the acme of it, and falls again at the close c When the mean arterial pressure is 100 cmm. Hg. before a meal, a the above example, the capillary blood-pressure will read, 20 c Hg. ; and in an hour after the meal, when the arterial pressure : to 115 cmm. Hg., or so, the capillary pressure will rise to at l 30 cmm Hg. Though this is a large relative rise, my observat show that it is not less than this, and that it is often more.

"On Reptilian Remains from the Trias of Elgin." By G. A. BOULENGER, F.R.S. Received April 29,—Read June 11, 1903.

(Abstract.)

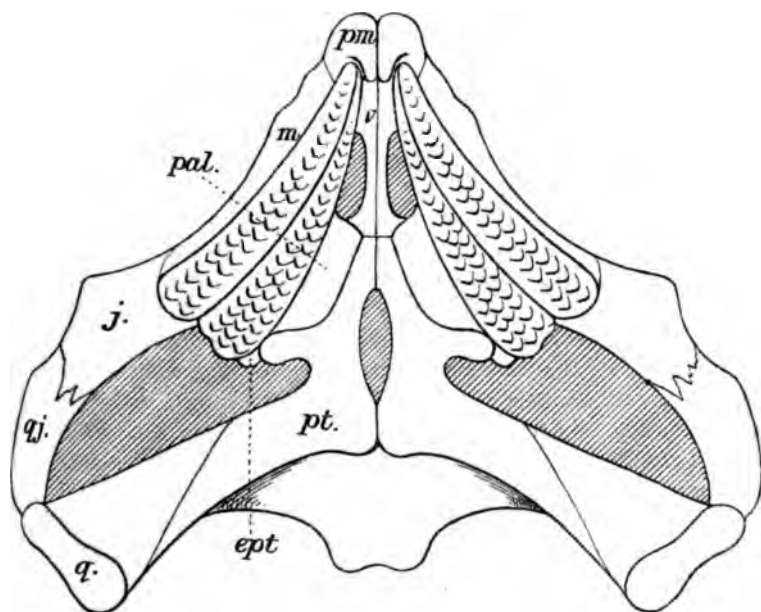
Descriptions are given of various reptilian remains obtained by Mr. William Taylor, J.P., of Lhanbryde, in the Triassic sandstone quarries at Lossiemouth, near Elgin. Thanks to the kind permission of Dr. A. S. Woodward, the fossils were further developed in the Geological Department of the British Museum by Mr. Hall.

The remains described belong to three different reptiles.

I. *HYPERODAPEDON GORDONI*, Huxley.

A skull is contained in a block of sandstone, split horizontally in the plane of the palate, which is for the first time clearly exposed.

FIG. 1.



*ep.* Ectopterygoid. *j.* Jugal. *m.* Maxilla. *pal.* Palatine. *pm.* Præmaxilla. *pt.* Pterygoid. *q.* Quadrate. *qj.* Quadratojugal. *r.* Vomer.

The structure of the palate is seen to have been very different from what Huxley had surmised and shows a much nearer approximation to that of *Sphenodon*. The choanæ were elongate, oval, and situated



between the palatines and the vomers at some distance behind the præmaxillaries. Doubts have been thrown on Huxley's interpretation of the outer toothed bone of the skull, and it is important to settle the question of its identification. The new material has convinced the author that the teeth in the upper jaw are borne by both the maxillary and the palatine, as stated by Huxley. The fossil shows well the elongate rhomboidal vacuity between the pterygoid, ending at the point where they converge before diverging again towards the quadrate, to the massive anterior branch of which they are suturally united.

As may be seen from the annexed restoration, the palate of *Hyperodapedon* bears great resemblance, in its general structure, to that of the living *Sphenodon*, the principal differences, apart from the dentition, residing in the smaller bony roof of the mouth and the narrower vomers.

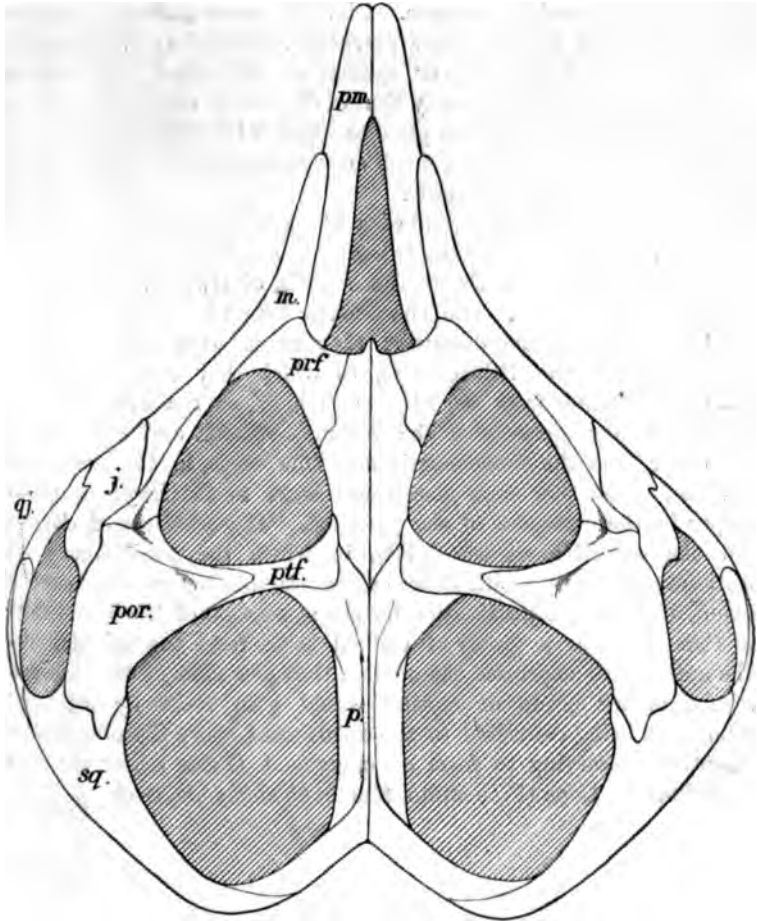
## II. STENOMETOPON TAYLORI, G. et sp. nn.

This name is proposed for a considerable portion of a skull of a Rhynchocephalian, closely related to *Hyperodapedon*, and belonging to the same family, Rhynchosauridæ. Its length is 177 mms. and its greatest width 160. One of the most striking features of *Hyperodapedon* as compared with its New Zealand ally, *Sphenodon*, resides in its much broader and more massive skull. The skull of the new Rhynchocephalian, although agreeing in its general structure with that of *Hyperodapedon*, is not broader and hardly more massive than that of *Sphenodon*, from which it differs, however, very much in shape. The rostrum has quite a different direction from either of these skulls, the tusk-like præmaxillaries, instead of being bent downwards into recurved processes, are directed forwards in a gradual slope from the frontal region to their extremities, which project beyond the turned-up extremities of the mandibular rami. This is practically the reverse of the condition in *Hyperodapedon*, where the strongly curved præmaxillary "tusks" are received between the outwardly directed rostral processes of the mandible. Nasal bones are absent.

As in *Hyperodapedon*, the nasal aperture is single, but, in accordance with the shape of the præmaxillaries, it is more elongate, its length being to its width as  $2\frac{1}{3} : 1$ ; its posterior border extends to the level of the orbits, which are entirely directed upwards. The inter-orbital region is narrow, especially behind. The supra-temporal fossæ are very large, separated from the orbits by the narrow post-orbital arch and from each other by the sharp median crest of the parietals. The latero-temporal fossa is kidney-shaped and proportionately larger than in *Hyperodapedon*, but smaller than the supra-temporal fossa. The maxillary bone is deep and nearly vertical, with an oblique ridge

extending downward and backward to the jugal; the maxillary teeth, so far as they are preserved, appear very similar to those of *Hypero-*

FIG. 2.



*j.* Jugal. *m.* Maxilla. *p.* Parietal. *pm.* Præmaxilla. *por.* Postorbital.  
*prf.* Præfrontal. *pm.* Præmaxilla. *ptf.* Postfrontal. *qj.* Quadratojugal  
*sq.* Squamosal.

*dapedon*, and form a single series in front and two behind. The palate is imperfectly preserved, but what is left of it agrees in essential points with *Hyperodapedon*; the palatine teeth are disposed in three series behind.

## III. ORNITHOSUCHUS WOODWARDI, E. T. Newton.

The specimen on which this species was founded by Mr. Newton in 1894, indicated a reptile about  $2\frac{3}{4}$  feet long. Specimens more than twice as large are now described, and afford much information on points which remained obscure. Clavicles were present, large and widely expanded at their inner extremity, where they overlapped the inter-clavicle. A plastron, or system of abdominal ribs, was also present, resembling very closely that of *Sphenodon*, each segment being formed of a median angulate piece to which a lateral limb is attached, the segments, however, being much more numerous and closer together than in the New Zealand reptile.

The presence of clavicles and of a plastron show that *Ornithosuchus* cannot be included among the Dinosaurs, as originally suggested, but must be placed in the Order Thecodontia, of Owen, which contains *Belodon* and *Aëtosaurus*. The Thecodontia should be kept distinct from the Crocodilia or Emydosauria; they agree with the latter, the Dinosauria and the Pelycosauria, to which they are very closely related, and differ from the Rhynchocephalia, in the truly thecodont dentition; they agree with the Rhynchocephalia and Pelycosauria, and differ from the Emydosauria and Dinosauria, in the presence of clavicles, whilst they show close resemblance to the Rhynchocephalia proper in the structure of the plastron. The presence of clavicles and the condition of the pelvis, in which the pubis enters the acetubulum, together with other characters showing greater generalisation, afford ample justification for the separation of the Thecodontia or Parasuchia, as a group of ordinal rank, from the Emydosauria. The author also expresses the opinion that precision in the definition of the higher group of reptiles would gain much by the Order Dinosauria being restricted to the carnivorous, truly thecodont forms, the others deserving to form an equivalent Order under the name of Orthopoda, Cope (*Predentata*, Marsh, *Ornithischia*, Seeley).

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"The Bending of Electric Waves round a Conducting Obstacle:  
Amended Result." By H. M. MACDONALD, M.A., F.R.S.  
Received May 12,—Read June 11, 1903.

I have recently (May 3) received an intimation from the Secretaries of the Royal Society that Lord Rayleigh has questioned the validity of my analysis\* of the problem of bending of electric waves round a conducting obstacle, the ground of the criticism being that the shortness of the wave-length involves that the important harmonics in the expansion are of high order comparable with the ratio of the circumference of the sphere to the wave-length, and that for them the approximations in the paper are not valid. Subsequently I have learned that M. Poincaré has made a similar objection.

I have at once to admit the validity of the objection thus raised. As it appears that it is still to some degree uncertain what phenomena would be indicated by theory, I venture to submit the following correction and development of my analysis, which gives a solution of the problem agreeing with Lord Rayleigh's anticipation (p. 40, *supra*).

Starting from the expression for  $\partial\psi/\partial\mu_{r=a}$ , given on p. 254,

$$\frac{\partial\psi}{\partial\mu_{r=a}} = \frac{\partial}{\partial\mu} \sum_1^{\infty} g_n(r_1) \left[ a^1 J_{n+1}(\kappa a) - \frac{a^1 K_{n+1}(\iota\kappa a)}{\frac{\partial}{\partial a} \{a^1 K_{n+1}(\iota\kappa a)\}} \frac{\partial}{\partial a} \{a^1 J_{n+1}(\kappa a)\} \right] (1 - \mu^2) \frac{\partial P_n}{\partial\mu},$$

it may be written

$$\begin{aligned} \frac{\partial\psi}{\partial\mu_{r=a}} = & \frac{\partial}{\partial\mu} \sum_1^{\infty} g_n(r_1) \left[ a^1 J_{n+1}(\kappa a) + \frac{1}{\iota\kappa} \frac{\partial}{\partial a} \{a^1 J_{n+1}(\kappa a)\} \right] (1 - \mu^2) \frac{\partial P_n}{\partial\mu} \\ & - \frac{\partial}{\partial\mu} \sum_1^{\infty} g_n(r_1) \left[ \frac{a^1 K_{n+1}(\iota\kappa a)}{\frac{\partial}{\partial a} \{a^1 K_{n+1}(\iota\kappa a)\}} + \frac{1}{\iota\kappa} \right] \frac{\partial}{\partial a} \{a^1 J_{n+1}(\kappa a)\} (1 - \mu^2) \frac{\partial P_n}{\partial\mu}; \end{aligned}$$

that is

$$\frac{\partial\psi}{\partial\mu_{r=a}} = \frac{\partial}{\partial\mu} \left[ f(a) + \frac{1}{\iota\kappa} \frac{\partial}{\partial a} \{f'(a)\} \right] - S,$$

where

$$S = \frac{\partial}{\partial\mu} \sum_1^{\infty} g_n(r_1) \left[ \frac{a^1 K_{n+1}(\iota\kappa a)}{\frac{\partial}{\partial a} \{a^1 K_{n+1}(\iota\kappa a)\}} + \frac{1}{\iota\kappa} \right] \frac{\partial}{\partial a} \{a^1 J_{n+1}(\kappa a)\} (1 - \mu^2) \frac{\partial P_n}{\partial\mu}.$$

Writing

$$\kappa a = z, \quad a^1 J_{n+1}(z) = \sqrt{\frac{2}{\pi}} u_n(z), \quad a^1 J_{-n-1}(z) = (-)^n \sqrt{\frac{2}{\pi}} v_n(z),$$

\* 'Roy. Soc. Proc.,' vol. 71, p. 251.

then

$$z^{\frac{1}{2}} K_{n+\frac{1}{2}}(z) = \frac{\pi e^{-(n+\frac{1}{2})\pi i}}{2 \sin(n+\frac{1}{2})\pi} [z^{\frac{1}{2}} J_{-n-\frac{1}{2}}(z) - e^{(n+\frac{1}{2})\pi i} z^{\frac{1}{2}} J_{n+\frac{1}{2}}(z)],$$

that is

$$z^{\frac{1}{2}} K_{n+\frac{1}{2}}(z) = \sqrt{\frac{\pi}{2}} e^{-(n+\frac{1}{2})\pi i} \{v_n(z) - u_n(z)\},$$

$$\frac{\partial}{\partial z} \{z^{\frac{1}{2}} K_{n+\frac{1}{2}}(z)\} = \sqrt{\frac{\pi}{2}} e^{-(n+\frac{1}{2})\pi i} \{v_n'(z) - u_n'(z)\};$$

and putting

$$u_n(z) = R_n^{\frac{1}{2}}(z) \sin \phi_n, \quad v_n(z) = R_n^{\frac{1}{2}}(z) \cos \phi_n,$$

then

$$v_n'(z) - u_n'(z) = \frac{1}{2} \frac{R_n'(z)}{R_n^{\frac{1}{2}}(z)} e^{-\phi_n} - R_n^{\frac{1}{2}}(z) \frac{\partial \phi_n}{\partial z} e^{-\phi_n}.$$

Now

$$v_n(z) u_n'(z) - v_n'(z) u_n(z) = 1,$$

whence

$$R_n(z) \frac{\partial \phi_n}{\partial z} = 1,$$

therefore

$$v_n'(z) - u_n'(z) = \left\{ \frac{1}{2} R_n'(z) - 1 \right\} \frac{e^{-\phi_n}}{R_n^{\frac{1}{2}}(z)};$$

hence

$$\frac{a^{\frac{1}{2}} K_{n+\frac{1}{2}}(\kappa a)}{\frac{\partial}{\partial a} \{a^{\frac{1}{2}} K_{n+\frac{1}{2}}(\kappa a)\}} + \frac{1}{\kappa} = \left\{ \frac{R_n(z)}{\frac{1}{2} R_n'(z) - 1} + \frac{1}{1} \right\} \frac{1}{\kappa},$$

or

$$\frac{a^{\frac{1}{2}} K_{n+\frac{1}{2}}(\kappa a)}{\frac{\partial}{\partial a} \{a^{\frac{1}{2}} K_{n+\frac{1}{2}}(\kappa a)\}} + \frac{1}{\kappa} = \frac{1}{\kappa} \{1 - R_n(z) \cos \chi_n e^{\chi_n}\},$$

where

$$\tan \chi_n + \frac{1}{2} R_n'(z) = 0.$$

Again

$$\frac{\partial}{\partial a} \{a^{\frac{1}{2}} J_{n+\frac{1}{2}}(\kappa a)\} = \sqrt{\frac{2\kappa}{\pi}} u_n'(z),$$

that is

$$\frac{\partial}{\partial a} \{a^{\frac{1}{2}} J_{n+\frac{1}{2}}(\kappa a)\} = \sqrt{\frac{2\kappa}{\pi}} \left[ \frac{1}{2} \frac{R_n'(z)}{R_n^{\frac{1}{2}}(z)} \sin \phi_n + R_n^{\frac{1}{2}}(z) \cos \phi_n \frac{\partial \phi_n}{\partial z} \right],$$

or

$$\frac{\partial}{\partial a} \{a^{\frac{1}{2}} J_{n+\frac{1}{2}}(\kappa a)\} = \sqrt{\frac{2\kappa}{\pi}} \frac{\cos(\phi_n + \chi_n)}{R_n^{\frac{1}{2}}(z) \cos \chi_n}.$$

Further

$$g_n(r_1) = -\kappa r_1^{-1} e^{\pi i/4} \left\{ e^{(n-1)\pi i/2} K_{n-\frac{1}{2}}(\kappa r_1) + e^{(n+1)\pi i/2} K_{n+\frac{1}{2}}(\kappa r_1) \right\}, *$$

whence

$$g_n(r_1) = -\kappa r_1^{-1} e^{-(n+\frac{1}{2})\pi} \frac{2n+1}{\kappa r_1} K_{n+\frac{1}{2}}(\kappa r_1),$$

that is

$$g_n(r_1) = \frac{2n+1}{\kappa^{\frac{1}{2}} r_1^{\frac{3}{2}}} e^{-(n+\frac{1}{2})\pi} \sqrt{\frac{\pi}{2}} e^{-(n+\frac{1}{2})\pi} \{v_n(\kappa r_1) - u_n(\kappa r_1)\},$$

or

$$g_n(r_1) = -\frac{2n+1}{\kappa^{\frac{1}{2}} r_1^{\frac{3}{2}}} \sqrt{\frac{\pi}{2}} \{v_n(\kappa r_1) - u_n(\kappa r_1)\}.$$

Hence

$$S = -\frac{\partial}{\partial \mu} \sum_1^{\infty} \frac{2n+1}{\kappa^{\frac{1}{2}} r_1^{\frac{3}{2}}} \sqrt{\frac{\pi}{2}} \{v_n(\kappa r_1) - u_n(\kappa r_1)\} \frac{1}{\kappa} \{1 - R_n(z) \cos \chi_n e^{i\chi_n}\} \\ \sqrt{\frac{2\kappa}{\pi} \frac{\cos(\phi_n + \chi_n)}{R_n^{\frac{1}{2}}(z) \cos \chi_n}} (1 - \mu^2) \frac{\partial P_n}{\partial \mu},$$

that is

$$S = -\frac{\iota}{\kappa r_1^2} \frac{\partial}{\partial \mu} \sum_1^{\infty} (2n+1) \{v_n(\kappa r_1) - u_n(\kappa r_1)\} \{1 - R_n(z) \cos \chi_n e^{i\chi_n}\} \\ \frac{\cos(\phi_n + \chi_n)}{R_n^{\frac{1}{2}}(z) \cos \chi_n} (1 - \mu^2) \frac{\partial P_n}{\partial \mu},$$

or

$$S = -\frac{\iota}{\kappa r_1^2} \sum_1^{\infty} n(n+1)(2n+1) \{v_n(\kappa r_1) - u_n(\kappa r_1)\} \{1 - R_n(z) \cos \chi_n e^{i\chi_n}\} \\ \frac{\cos(\phi_n + \chi_n)}{R_n^{\frac{1}{2}}(z) \cos \chi_n} P_n.$$

Now for values of  $\theta$  ( $= \cos^{-1}\mu$ ) which are not near to 0 or  $\pi$ ,  $P_n$  may be replaced by  $\sqrt{\frac{2}{\pi n}} \cos \left\{ \left(n + \frac{1}{2}\right) \theta - \frac{\pi}{4} \right\}$  for large values of  $n$ ; further, for values of  $n$  small compared with  $z$ , neglecting small quantities,  $\chi_n$  is zero and  $R_n(z)$  is unity. Hence

$$S = -\frac{\iota}{\kappa r_1^2} \sum_{n_0}^{\infty} n(n+1)(2n+1) \{v_n(\kappa r_1) - u_n(\kappa r_1)\} \{1 - R_n(z) \cos \chi_n e^{i\chi_n}\} \\ \frac{\cos(\phi_n + \chi_n)}{R_n^{\frac{1}{2}}(z) \cos \chi_n} \sqrt{\frac{2}{\pi n \sin \theta}} \cos \left\{ \left(n + \frac{1}{2}\right) \theta - \frac{\pi}{4} \right\},$$

where  $n_0$  is large, but not comparable with  $z$ . Since  $\theta$  is not small,  $\kappa r_1$  may be replaced by  $z$ , and then

$$S = -\frac{\iota}{\kappa a^2} \sum_{n_0}^{\infty} n(n+1)(2n+1) \sqrt{\frac{2}{\pi n \sin \theta}} \{1 - R_n(z) \cos \chi_n e^{i\chi_n}\} \\ \frac{\cos(\phi_n + \chi_n)}{\cos \chi_n} e^{-i\phi_n} \cos \left\{ \left(n + \frac{1}{2}\right) \theta - \frac{\pi}{4} \right\},$$

that is

$$S = -\frac{i}{2\kappa a^2} \sum_{n_0}^{\infty} n(n+1)(2n+1) \sqrt{\frac{2}{\pi n \sin \theta}} \{1 - R_n(z) \cos \chi_n e^{i\chi_n}\}$$

$$\frac{e^{-i\phi_n}}{\cos \chi_n} \left[ \cos \left\{ \phi_n + \chi_n + (n + \frac{1}{2}) \theta - \frac{\pi}{4} \right\} + \cos \left\{ \phi_n + \chi_n - (n + \frac{1}{2}) \theta + \frac{\pi}{4} \right\} \right]$$

Writing

$$\frac{R_n(z)}{4\kappa a^2} \sqrt{\frac{2}{\pi n \sin \theta}} n(n+1)(2n+1) = f_1(n),$$

$$\frac{i}{4\kappa a^2 \cos \chi_n} \sqrt{\frac{2}{\pi n \sin \theta}} n(n+1)(2n+1) = f_2(n),$$

the above becomes

$$S = S_1 + S_2 + S_3 + S_4 - S_5 - S_6 - S_7 - S_8,$$

where

$$S_1 = \sum_{n_0}^{\infty} f_1(n) e^{i \left\{ 2\chi_n + (n + \frac{1}{2}) \theta - \frac{\pi}{4} \right\}}, \quad S_5 = \sum_{n_0}^{\infty} f_2(n) e^{i \left\{ \chi_n + (n + \frac{1}{2}) \theta - \frac{\pi}{4} \right\}},$$

$$S_2 = \sum_{n_0}^{\infty} f_1(n) e^{i \left\{ 2\chi_n - (n + \frac{1}{2}) \theta + \frac{\pi}{4} \right\}}, \quad S_6 = \sum_{n_0}^{\infty} f_2(n) e^{i \left\{ \chi_n - (n + \frac{1}{2}) \theta + \frac{\pi}{4} \right\}},$$

$$S_3 = \sum_{n_0}^{\infty} f_1(n) e^{-i \left\{ 2\phi_n + (n + \frac{1}{2}) \theta - \frac{\pi}{4} \right\}}, \quad S_7 = \sum_{n_0}^{\infty} f_2(n) e^{-i \left\{ 2\phi_n + \chi_n + (n + \frac{1}{2}) \theta - \frac{\pi}{4} \right\}},$$

$$S_4 = \sum_{n_0}^{\infty} f_1(n) e^{-i \left\{ 2\phi_n - (n + \frac{1}{2}) \theta + \frac{\pi}{4} \right\}}, \quad S_8 = \sum_{n_0}^{\infty} f_2(n) e^{-i \left\{ 2\phi_n + \chi_n - (n + \frac{1}{2}) \theta + \frac{\pi}{4} \right\}}.$$

If any value of  $n_1$  of  $n$  be chosen, and  $n$  is written  $n_1 + \nu$ , the quantities  $\chi_n$ ,  $\phi_n$  can be expressed in the form  $A_0 + A_1 \frac{\nu}{z} + A_2 \frac{\nu^2}{z^2} + \dots$

for values of  $\nu$  for which the series converge; similarly for  $f_1(n)$ ,  $f_2(n)$ . The group of terms in any of the series  $S_1$  etc., for which this holds for  $n_1$ , will contribute nothing to the result unless the coefficient of  $\nu$  in the exponent vanishes; also when the coefficient of  $\nu$  in the exponent vanishes and the coefficient of  $\nu^2$  does not, the sum of the corresponding group of terms

$$\sum \left( A_0 + A_1 \frac{\nu}{2} + \dots \right) e^{i \left( B_0 \nu + B_2 \frac{\nu^2}{2} + \dots \right)}$$

is

$$A_0 \sqrt{\frac{\pi z}{|B_2|}} e^{i \left( B_0 \nu \pm \frac{\pi}{4} \right)},$$

the upper or lower sign being taken according as  $B_2$  is positive or negative.\*

\* Lorenz, 'Œuvres Scientifiques,' vol. 1, p. 425.

Now it may be shown that

$$R_n(z) = \sum_{s=0}^{\infty} \frac{\Pi(n+s)\Pi(s-\frac{1}{2})}{\Pi(n-s)\Pi(s)\Pi(-\frac{1}{2})} \frac{1}{z^{2s}},$$

and hence that

$$R_n(z) = \frac{z}{\sqrt{z^2 - (n + \frac{1}{2})^2}},$$

as long as  $z > n + \frac{1}{2}$  and  $z - (n + \frac{1}{2})$  is of higher order than  $z^{\frac{1}{2}}$ ; also from the relation

$$R_n \frac{\partial \phi_n}{\partial z} = 1,$$

it follows that

$$\phi_n = \sqrt{z^2 - (n + \frac{1}{2})^2} - \frac{n\pi}{2} + (n + \frac{1}{2}) \sin^{-1} \frac{n + \frac{1}{2}}{z},$$

subject to the same limitations. Further, when  $z - (n + \frac{1}{2})$  is of a lower order than  $z^{\frac{1}{2}}$ ,

$$R_n(z) = \frac{(n + \frac{1}{2})^{\frac{1}{2}}}{3^{\frac{1}{2}} \sqrt{\pi}} \left[ \Pi(-\frac{5}{6}) + \Pi(-\frac{1}{2})(n + \frac{1}{2} - z) \left( \frac{24}{n + \frac{1}{2}} \right)^{\frac{1}{2}} \right. \\ \left. + \Pi(-\frac{1}{6})(n + \frac{1}{2} - z)^2 \left( \frac{24}{n + \frac{1}{2}} \right)^{\frac{3}{2}} + \dots \right],$$

$$\phi_n = \frac{\pi}{6} + R_n(z - n - \frac{1}{2}) - \frac{R'_n(z - n - \frac{1}{2})^2}{R_n^2} + \dots,$$

where  $R_n, R'_n, \dots$  denote the values of  $R_n(z), R'_n(z), \dots$  when  $z = n + \frac{1}{2}$ . When  $n + \frac{1}{2} > z$ , writing

$$u_n(z) = T_n(z) e^{\tau_n}, \quad v_n(z) = T_n(z) e^{-\tau_n},$$

$$2T_n(z) = \frac{z}{\sqrt{(n + \frac{1}{2})^2 - z^2}},$$

as long as  $n + \frac{1}{2} > z$  and  $n + \frac{1}{2} - z$  is of a higher order than  $z^{\frac{1}{2}}$ ; also

$$\tau_n = -\frac{1}{2} \log 2 + (n + \frac{1}{2}) \log \frac{n + \frac{1}{2} - \sqrt{(n + \frac{1}{2})^2 - z^2}}{z} + \sqrt{(n + \frac{1}{2})^2 - z^2};$$

and when  $n + \frac{1}{2} - z$  is of a lower order than  $z^{\frac{1}{2}}$ ,

$$2T_n(z) = \frac{z^{\frac{1}{2}}}{3^{\frac{1}{2}} \sqrt{\pi}} \left[ \Pi(-\frac{5}{6}) \sin \frac{\pi}{3} + \Pi(-\frac{1}{2}) \sin \frac{3\pi}{3} (n + \frac{1}{2} - z) \left( \frac{24}{z} \right)^{\frac{1}{2}} \right. \\ \left. + \Pi(-\frac{1}{6}) \sin \frac{5\pi}{3} (n + \frac{1}{2} - z)^2 \left( \frac{24}{z} \right)^{\frac{3}{2}} + \dots \right]$$

$$\tau_n = -\frac{1}{4} \log 3 + \frac{1}{2T_n} (z - n - \frac{1}{2}) - \frac{T'_n}{2T_n^2} (z - n - \frac{1}{2})^2 + \dots,$$



where  $T_n, T_n', \dots$  denote the values of  $T_n(z), T_n'(z), \dots$ , when  $z = n + \frac{1}{2}$ .\*

From the expression for  $R_n(z)$  it follows that

$$\frac{1}{2}R_n'(z) = - \sum_{s=1}^{\infty} \frac{\Pi(n+s) \Pi(s-\frac{1}{2})}{\Pi(n-s) \Pi(s-1) \Pi(-\frac{1}{2})} \frac{1}{z^{2s+1}},$$

hence  $\tan \chi_n$  is positive and increases with  $n$ , thus  $\chi_n$  lies between 0 and  $\frac{1}{2}\pi$  and  $\partial \chi_n / \partial n$  is positive; therefore  $S_1$  and  $S_5$  both vanish. When  $z - (n + \frac{1}{2})$  is of higher order than  $z^{\frac{1}{2}}$

$$R_n'(z) = \frac{-(n + \frac{1}{2})^2}{\{z^2 - (n + \frac{1}{2})^2\}^{\frac{3}{2}}},$$

hence

$$\tan \chi_n = \frac{1}{2} \frac{(n + \frac{1}{2})^2}{\{z^2 - (n + \frac{1}{2})^2\}^{\frac{3}{2}}},$$

and

$$\sec^2 \chi_n \frac{\partial \chi_n}{\partial n} = \frac{n + \frac{1}{2}}{\{z^2 - (n + \frac{1}{2})^2\}^{\frac{3}{2}}} + \frac{3}{2} \frac{(n + \frac{1}{2})^2}{\{z^2 - (n + \frac{1}{2})^2\}^{\frac{5}{2}}},$$

therefore as  $n$  increases, subject to the limitation that  $z - (n + \frac{1}{2})$  is of higher order than  $z^{\frac{1}{2}}$ ,  $R_n(z)$  tends to become of the order  $(n + \frac{1}{2})^{\frac{1}{2}}$ ,  $R_n'(z)$  of the order unity, and  $\partial \chi_n / \partial n$  of the order  $(n + \frac{1}{2})^{-\frac{1}{2}}$ . When  $z - (n + \frac{1}{2})$  is of lower order than  $z^{\frac{1}{2}}$ , it follows from the relation

$$R_n(z) = \frac{(n + \frac{1}{2})^{\frac{1}{2}}}{3^{\frac{1}{2}} \sqrt{\pi}} \left[ \Pi(-\frac{1}{6}) + \Pi(-\frac{1}{2})(n + \frac{1}{2} - z) \left( \frac{24}{n + \frac{1}{2}} \right)^{\frac{1}{2}} + \dots \right]$$

that  $R_n(z)$  is of the order  $(n + \frac{1}{2})^{\frac{1}{2}}$ ,  $R_n'(z)$  of the order unity, and  $\partial \chi_n / \partial n$  of the order  $(n + \frac{1}{2})^{-\frac{1}{2}}$ . These latter conditions also hold when  $n + \frac{1}{2} - z$  is of lower order than  $z^{\frac{1}{2}}$ . When  $n + \frac{1}{2} - z$  is of higher order than  $z^{\frac{1}{2}}$ ,  $R_n(z)$  is given by

$$R_n(z) = 2T_n(z) \cosh 2\tau_n,$$

and

$$R_n'(z) = 2T_n'(z) \cosh 2\tau_n + 4T_n(z) \sinh 2\tau_n \frac{\partial \tau_n}{\partial z},$$

that is

$$R_n'(z) = 2T_n'(z) \cosh 2\tau_n + 2 \sinh 2\tau_n,$$

whence

$$\begin{aligned} -2 \sec^2 \chi_n \frac{\partial \chi_n}{\partial n} &= 2 \frac{\partial T_n'(z)}{\partial n} \cosh 2\tau_n + 4T_n'(z) \sinh 2\tau_n \frac{\partial \tau_n}{\partial n} \\ &\quad + 4 \cosh 2\tau_n \frac{\partial \tau_n}{\partial n}; \end{aligned}$$

now

$$2T_n'(z) = \frac{(n + \frac{1}{2})^2}{\{(n + \frac{1}{2})^2 - z^2\}^{\frac{3}{2}}},$$

\* These results are given by Lorenz, 'Œuvres Scientifiques,' vol. 1, pp. 435-479.

therefore  $2 \frac{\partial T_n'(z)}{\partial n}$  is negative and at most of the order  $(n + \frac{1}{2})^{-1}$ ,  $T_n'(z)$  being at most of the order unity; further, when  $z = n + \frac{1}{2}$ ,  $\tau_n = -\frac{1}{4} \log 3$ , and as  $n$  increases  $T_n$  diminishes rapidly, hence  $\cosh 2\tau_n \cos^2 \chi_n$  and  $\sinh 2\tau_n \sin^2 \chi_n$  are less than unity and diminish rapidly as  $n$  increases; also writing  $n + \frac{1}{2} = z \cosh \delta$ ,

$$\tau_n = -\frac{1}{2} \log 2 - z \delta \cosh \delta + z \sin \delta,$$

$$\frac{\partial \tau_n}{\partial n} = -\delta,$$

hence, unless  $\delta$  is small,  $\tau_n$  is a large negative quantity, and therefore  $\cosh 2\tau_n \cos^2 \chi_n$ ,  $\sinh 2\tau_n \sin^2 \chi_n$ , by the above, very small, whence it follows that  $\partial \chi_n / \partial n$  is always very small. The series  $S_2$  and  $S_6$  therefore both vanish.

It is known that neither  $u_n(z)$  or  $v_n(z)$  can vanish for a value of  $n$ , which satisfies the condition that  $n + \frac{1}{2} > \frac{2z}{\pi}$ , and the last time  $v_n(z)$  vanishes as  $n$  increases the value of  $\phi_n$  is  $\frac{1}{2} \pi$ ; as  $n$  increases farther  $\phi_n$  diminishes to zero. When  $z - (n + \frac{1}{2})$  is of higher order than  $z^{\frac{1}{2}}$ , writing  $n + \frac{1}{2} = z \sin \alpha$ , where  $\frac{1}{2} \pi > \alpha > 0$ ,

$$\phi_n = z \cos \alpha - \frac{1}{2} n \pi + (n + \frac{1}{2}) \alpha,$$

$$\frac{\partial \phi_n}{\partial n} = \alpha - \frac{1}{2} \pi, \quad \frac{\partial^2 \phi_n}{\partial n^2} = \frac{1}{z \cos \alpha}.$$

hence  $\frac{\partial \phi_n}{\partial n}$  is negative, and as  $n$  increases  $-\frac{\partial \phi_n}{\partial n}$  diminishes and tends

to the order  $(n + \frac{1}{2})^{-\frac{1}{2}}$ . When  $z - (n + \frac{1}{2})$  is of lower order than  $z^{\frac{1}{2}}$ ,  $\frac{\partial \phi_n}{\partial n}$  is given by

$$\frac{\partial \phi_n}{\partial n} = -\frac{1}{R_n} + (z - n - \frac{1}{2}) \frac{R'_n}{R_n^2} + \dots,$$

whence, remembering that  $R'_n$  is negative and  $R_n$  is of the order  $(n + \frac{1}{2})^{\frac{1}{2}}$ ,  $\frac{\partial \phi_n}{\partial n}$  is negative and of the order  $(n + \frac{1}{2})^{-\frac{1}{2}}$ . When  $n + \frac{1}{2} > z$ ,

using the relation  $\tan \phi_n = e^{2\tau_n}$ ,

$$\sec^2 \phi_n \frac{\partial \phi_n}{\partial n} = 2e^{2\tau_n} \frac{\partial \tau_n}{\partial n},$$

and therefore

$$\frac{\partial \phi_n}{\partial n} = -\frac{2\delta e^{4\tau_n}}{1 + e^{4\tau_n}},$$

where

$$z \cosh \delta = n + \frac{1}{2},$$

hence  $\frac{\partial \phi_n}{\partial n}$  is negative, and  $-\frac{\partial \phi_n}{\partial n}$  diminishes as the absolute value of  $n$  increases, therefore  $-\frac{\partial \phi_n}{\partial n}$  is, when  $n + \frac{1}{2} > 0$ , at most of an order  $(n + \frac{1}{2})^{-1}$ . Since  $\frac{\partial \phi_n}{\partial n}$  is always negative the series  $S_4$  vanishes, and since  $\frac{\partial \phi_n}{\partial n}$  is always negative, and  $\frac{\partial \chi_n}{\partial n}$  is always very small, the series  $S_8$  vanishes.

It remains to evaluate the series  $S_3$  and  $S_7$ . Writing  $n = n_1$  the exponent in the series  $S_3$  becomes

$$-i \left( 2\phi_{n_1} + 2 \frac{\partial \phi_{n_1}}{\partial n_1} v + \frac{\partial^2 \phi_{n_1}}{\partial n_1^2} v^2 + \dots + (n_1 + \frac{1}{2}) + v\theta - \frac{\pi}{4} \right),$$

and the coefficient of  $v$  in this vanishes, if

$$2 \frac{\partial \phi_{n_1}}{\partial n_1} + \theta = 0,*$$

and putting  $n_1 + \frac{1}{2} = z \sin \alpha$ , this becomes

$$2\alpha - \pi + \theta = 0,$$

and the sum of the corresponding group of terms in the series  $S_3$  is

$$f_1(n_1) \sim \sqrt{\frac{\pi}{\partial^2 \phi_{n_1}}} e^{-i \{ 2\phi_{n_1} + (n_1 + \frac{1}{2})\theta \}};$$

now

$$\phi_{n_1} = z \cos \alpha - \frac{1}{2} n_1 \pi + (n_1 + \frac{1}{2}) z,$$

that is

$$2\phi_{n_1} + (n_1 + \frac{1}{2})\theta = 2z \cos \alpha - n_1 \pi + (2n_1 + 1) z + (n_1 + \frac{1}{2}) \theta,$$

whence

$$2\phi_{n_1} + (n_1 + \frac{1}{2})\theta = 2z \cos \alpha + \frac{1}{2}\pi,$$

and the sum of the group of terms, therefore, is

$$f_1(n_1) \sim \sqrt{\pi z \cos \alpha} e^{-i (2z \cos \alpha + \frac{1}{2}\pi)},$$

that is, since, neglecting all but the terms of highest order,

$$f_1(n_1) = \frac{i}{4\kappa a^2 \cos \alpha} \sqrt{\frac{2}{\pi z \sin \alpha \sin \theta}} 2z^3 \sin^3 \alpha,$$

$$S_3 = \frac{\kappa^2 a \cos^2 \frac{1}{2}\theta}{2 \sin \frac{1}{2}\theta} e^{-2i\kappa a \sin \frac{1}{2}\theta}$$

\* This equation cannot be satisfied, by the preceding, for a value  $n_1$  of  $n$ , which is not such that  $z - (n + \frac{1}{2})$  is positive and of higher order than  $z^{\frac{1}{2}}$ .

Similarly the value of  $n$ , for which a group of terms of  $S_7$  has a value different from zero, is given by

$$2 \frac{\partial \phi_n}{\partial n} + \frac{\partial \chi_n}{\partial n} + \theta = 0,$$

and remembering that  $\frac{\partial \chi_n}{\partial n}$  is always very small, the corresponding value of  $n$  is  $n_1$  as in the previous case. Now, when  $n_1 + \frac{1}{2} = \pm \sin \alpha$ ,

$$\tan \chi_n = \frac{\sin^2 \alpha}{\pm \cos^2 \alpha},$$

and is, therefore, to the order required, zero,  $\cos \chi_n$  being unity, hence

$$S_7 = \frac{1}{2} \kappa^2 a \cos^2 \frac{1}{2} \theta e^{-2\kappa a \sin \frac{1}{2} \theta},$$

therefore

$$S = \frac{\kappa^2 a \cos^2 \frac{1}{2} \theta}{2 \sin \frac{1}{2} \theta} (1 - \sin \frac{1}{2} \theta).$$

The value of  $\frac{\partial \psi}{\partial \mu_{r=a}}$  is, therefore, for values of  $\theta$  which are not near to 0 or  $\pi$ , given by

$$\frac{\partial \psi}{\partial \mu_{r=a}} = \frac{\partial}{\partial \mu} \left[ f(a) + \frac{1}{\kappa} \frac{\partial}{\partial a} \{ f(a) \} \right] - \frac{\kappa' a \cos^2 \frac{1}{2} \theta}{2 \sin \frac{1}{2} \theta} (1 - \sin \frac{1}{2} \theta),$$

the terms of highest order only being retained. Now

$$f(a) = \frac{a^2 (1 - \mu^2)}{R_0} \frac{\partial}{\partial R_0} \frac{e^{-\kappa R_0}}{R_0}, *$$

where

$$R_0^2 = a^2 + r_1^2 - 2ar_1\mu,$$

that is,

$$f(a) = -\kappa \frac{a^2 (1 - \mu^2)}{R_0^2} e^{-\kappa R_0},$$

to the order adopted, and

$$\frac{\partial}{\partial \mu} \left[ f(a) + \frac{1}{\kappa} \frac{\partial}{\partial a} \{ f(a) \} \right] = -\frac{\partial}{\partial \mu} \frac{\kappa a^2 (1 - \mu^2)}{R_0^2} \left( 1 - \frac{a - r_1 \mu}{R_0} \right) e^{-\kappa R_0},$$

or

$$\frac{\partial}{\partial \mu} \left[ f(a) + \frac{1}{\kappa} \frac{\partial}{\partial a} \{ f(a) \} \right] = \frac{\kappa^2 a^2 r_1}{R_0^3} (1 - \mu^2) \left( 1 - \frac{a - r_1 \mu}{R_0} \right) e^{-\kappa R_0},$$

which for values of  $\theta$  not near to zero, becomes on putting  $r_1 = a$ ,

$$\frac{\partial}{\partial \mu} \left[ f(a) + \frac{1}{\kappa} \frac{\partial}{\partial a} \{ f(a) \} \right] = \frac{\kappa^2 a \cos^2 \frac{1}{2} \theta}{2 \sin \frac{1}{2} \theta} (1 - \sin \frac{1}{2} \theta).$$

\* 'Roy. Soc. Proc.' vol. 71, p. 251.

Therefore, when  $\theta$  is not small,  $\frac{\partial \psi}{\partial \mu_{r=a}}$  vanishes to the first order at least, so that there is no first order effect at a point on the surface of the sphere which is at a finite angular distance from the oscillator.

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"On the Structure of Gold Leaf and the Absorption Spectrum of Gold." By J. W. MALLETT, F.R.S., Professor of Chemistry in the University of Virginia. Received May 22,—Read June 11. 1903.

(Abstract.)

Attention is drawn to numerous irregularly distributed black lines which are to be seen in gold leaf examined with the microscope by transmitted light. These lines are shown to depend on the presence of minute wires or threads of the metal, unconnected with its crystal-line structure, but produced in the process of gold beating by the stretching, along lines of weakness, of the animal membrane between sheets of which the gold is placed, thus developing minute trough-like wrinkles into which the soft metal is forced.

The results are given of an examination of the absorption spectrum—in the visible, ultra-violet and infra-red regions—of metallic gold in a finely divided condition, as found in gold-coloured glass, and as reduced from dilute aqueous solutions of its salts.

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"Note on the Effect of Extreme Cold on the Emanations of Radium." By Sir WILLIAM CROOKES, F.R.S., and Professor JAMES DEWAR, F.R.S. Received and read May 28, 1903.

As it seemed advisable to examine the action of extreme cold on the action of radium, the following experiments have been made, in continuation of work formerly done by either of us separately.

The first endeavour was to ascertain whether the scintillations produced by radium on a sensitive blende screen were affected by cold.

A small screen of blende with a morsel of radium salt close in front was sealed in a glass tube, and a lens was adjusted in front so that the scintillations could be seen. On dipping the whole into liquid air they grew fainter and soon stopped altogether. Some doubt was felt whether this might not have been caused (1) by the presence of liquid, (2) by the screen losing sensitiveness, or (3) by the radium ceasing to emit the heavy positive ions. To test this two tubes were made, in one of which the radium salt could be cooled without the screen, and in the other the screen could be cooled while the radium salt was at the ordinary temperature. The accompanying sketch explains their construction.

FIG 1.

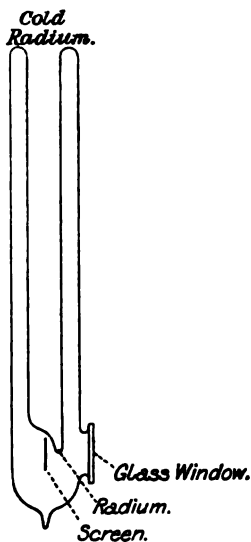
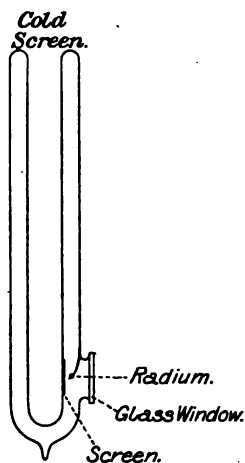


FIG. 2.



1. Radium salt cooled by liquid air, fig. 1. Screen at ordinary temperature. Scintillations quite as vigorous as with radium at the ordinary temperature, the screen and radium being *in vacuo*.

2. Radium at the ordinary temperature and screen cooled in liquid air, fig. 2. As the screen cooled the scintillations became fainter and at last could not be seen. On allowing the temperature to rise the scintillations recommenced.

3. A screen with a speck of radium salt in front of it was sealed in a tube. Water was put in the other end of the tube and the tube sealed on the pump. A good exhaustion was kept up and the water boiled away, the vapour being condensed in phosphoric anhydride. The tube was sealed off when a few fine drops of water were still remaining in the tube. The scintillations were well seen in this saturated aqueous vapour. The lower end of the tube was dipped in liquid air, which instantly condensed the aqueous vapour and left a very good vacuum. On now examining the scintillations they were if anything brighter and more vigorous than at first. When liquid hydrogen cooling was used instead of liquid air the action was equally marked, showing that the highest vacuum that can be obtained by the action of cold does not diminish the scintillations.

In the upper part of the tube, away from the radium and screen, two platinum wires were sealed to show the state of the vacuum. The spark passed easily at the ordinary temperature, showing a reddish line of aqueous vapour. When the other end of the tube was in liquid air the spark refused to pass.

4. It was thought that perhaps the passage of the induction spark might have liberated some occluded hydrogen, so another tube similar to the above was made without the platinum wires. Here also immersion in liquid air, if it had any effect, brightened the scintillations, and on replacing the liquid and cooling by liquid hydrogen no change was observable.

In order to test the activity of radium in rendering air electrically conductive, some radium bromide was sealed up in a glass tube and heated to the highest temperature the glass would stand, during the production of as high a vacuum as the mercurial pump would give. The whole tube was then immersed in liquid hydrogen contained in a vacuum vessel. On bringing the radium in such a vessel into a room in which a charged electroscope was placed, it began to leak when the tube of radium surrounded with liquid hydrogen was some 3 feet away, and was very rapid in its action when a foot away from the electrometer. On immersing the tube containing the liquid hydrogen with submerged radium in another large vessel of liquid air and bringing the combination near the electroscope the action was the same.

The luminosity of the radium salt in liquid hydrogen was much

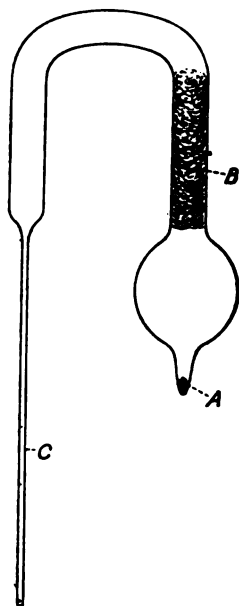
more marked with the pure compound than had been formerly observed with the diluted mixtures containing large quantities of barium salts.

Professor Rutherford and Mr. Soddy have made the important discovery that a condensible emanation is diffused into gases from solutions of radium salts, which is capable of condensation from the gas mixture at the temperature of liquid air. As it was important to ascertain what was taking place in this respect with the anhydrous radium bromide when isolated in the highest vacuum, the following experiment was arranged:—

A glass apparatus of the shape represented in fig. 3 was constructed.

The part marked C is a fine capillary drawn out tube some 5 or 6 inches in length, the B portion, about 2 inches long, being filled with hard-pressed purified asbestos. The radium salt was located at A, and the whole was most carefully heated, exhausted to the limit of the mercurial pump, and sealed off. In the dark no trace of phosphorescence could be seen in any part of the apparatus unless from the pieces of the radium bromide. The fine tube C was now immersed in liquid air in a large flask, so that distillation might proceed undisturbed for days. After 24 hours of this operation, on looking at the part C while covered with the liquid air, a marked phosphorescence was recognisable owing to some condensed emanation. The luminosity became naturally more marked the longer the time the action was allowed to proceed, and it is our intention to continue the experiments for a lengthened period of time, and then seal off the fine capillary part so that the condensed product may be thoroughly examined.

FIG. 3.





"The Evaporation of Water in a Current of Air." By EDGAR PHILIP PERMAN, Assistant Lecturer in the University College of South Wales and Monmouthshire. Communicated by Professor E. H. GRIFFITHS, F.R.S. Received February 4,—Read February 19, 1903.

*Introduction and Historical.*

It may be thought that so simple a matter as the evaporation of water in a current of air has already been thoroughly investigated, but, so far as I have been able to discover, this is not the case, although much concerning it has been taken for granted.

This research was undertaken in order to ascertain with what accuracy the vapour pressure of water could be calculated from the amount of water vapour carried off by an air current passed through the water, the temperature being maintained constant.

The work was begun in the Physikalisch-chemisches Institut, Leipzig, during the summer of 1902, and completed at University College, Cardiff, during the same year.

Experiments of a similar nature have been made by Regnault\* and by W. N. Shaw.† Regnault found that the weight of the vapour drawn off agreed within about 1 per cent. with that calculated from the vapour pressure. The temperatures employed extended up to 45° C.

Shaw's experiments were at ordinary temperatures of the air, and a very close agreement was found between the usually accepted vapour pressures and those calculated from the amount of water vapour drawn off.

*Description of Apparatus.*

The apparatus employed consisted of the following chief parts:—

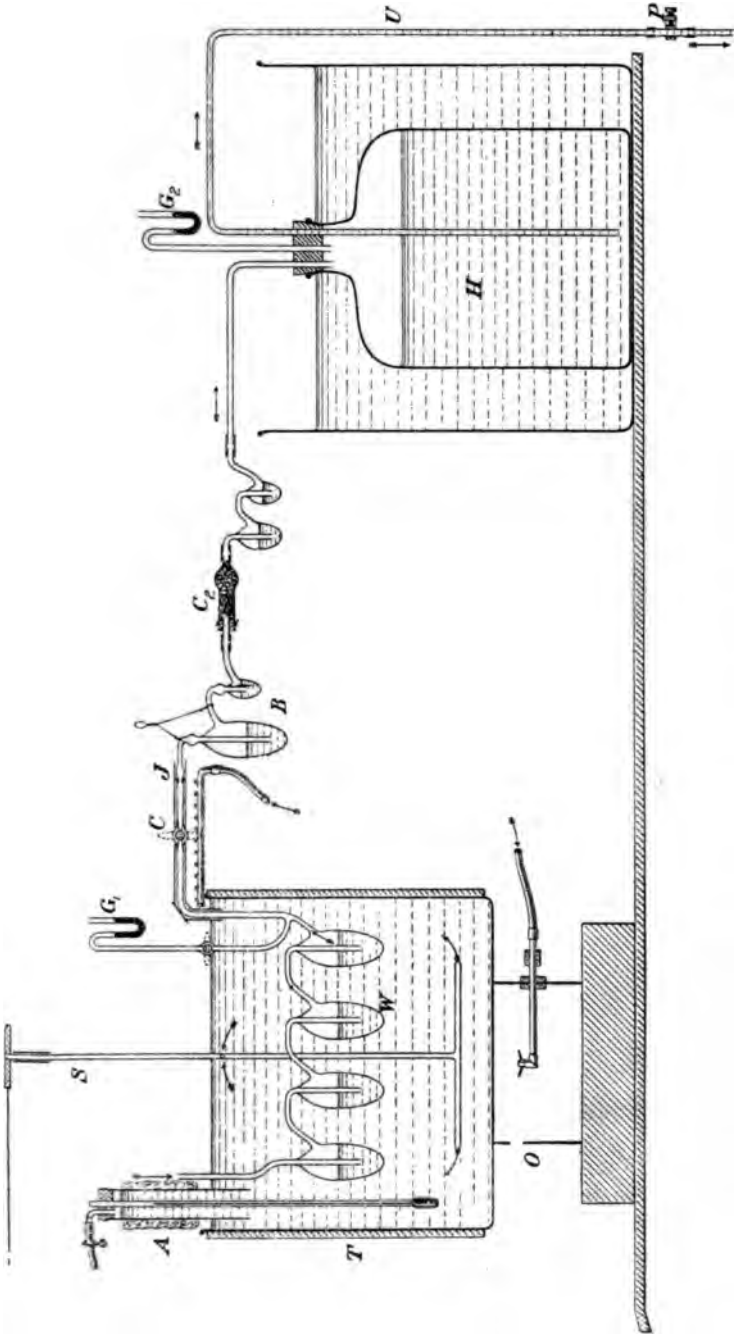
(1) Thermostat, with thermometer and stirring arrangement. (2) Four wash-bottles to contain the water. (3) Absorption apparatus to take up the water-vapour as the moist air passed through it. (4) Aspirator.

(1) The thermostat (T), consisted of an iron pot 23 cm. in diameter and 21 cm. high, surrounded by thick felt, and heated by an Ostwald burner (O), fig. 1. The thermometer was made by Fuess, of Berlin, and was standardised at the Reichsanstalt, Charlottenburg, number 17,000. It was divided into tenths of 1° C., and was read to 0.01°; the final corrections were also given to 0.01°. At the lower temperatures the stem was allowed to project from the bath just enough to make the thermometer readable, but at

\* 'Mem. de l'Acad.,' vol. 26, p. 679.

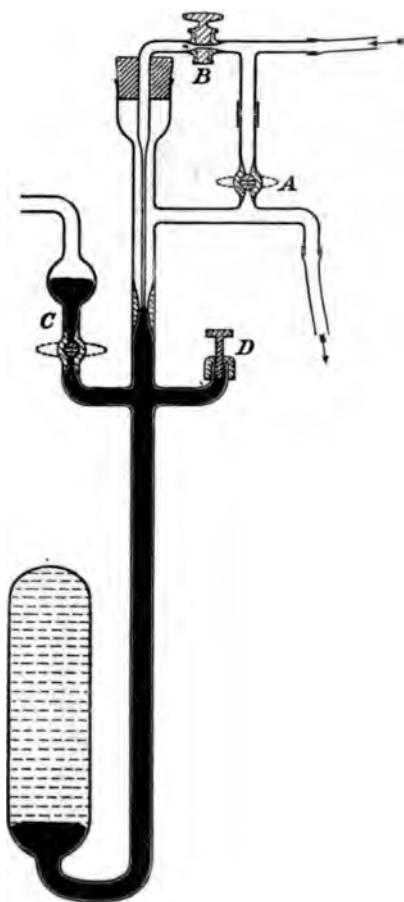
† 'Phil. Trans.,' A, vol. 179, 1888, Appendix No. III, p. 41.

FIG. 1.



the higher temperatures it was surrounded by a wide tube at the lower end, and closed by a cork at the upper end. It was wrapped round with a thick layer of cotton wool. The instrument is shown in fig. 1, A. The liquid could be drawn up from the bath into the wide tube by means of a small tube passing through the

FIG. 2.



A, B, fig. 2. The quantity of mercury enclosed can be adjusted to suit any temperature over a wide range by means of the bulb stop-cock beneath it, while, by means of the screw D, the temperature can be regulated to  $0.01^\circ$ , and can be easily brought to any point.\*

\* For details of the usual pattern of toluol regulator, see 'Physikalische Messungen, Ostwald-Luther,' p. 88.

cork; the tube was then drawn up by means of a clip on the tube connected with the bath tube. The temperature of the liquid in the wide tube was sufficiently uniform by convection currents. This was to be the case by emptying the liquid into the bath, and drawing up a fresh portion of the liquid. The reading of the thermometer remained unaltered. In the experiments the thermometer was placed in a position (in order to immerse the whole column into the bath) that in that case a correction for internal pressure was made and calculated from the data given in the certificate. The gas regulator was employed as shown in fig. 1), which maintained the temperature constant to  $0.01^\circ$ ; it rarely varied more than this during the experiment, and I do not think that the temperature exceeds  $0.02^\circ$  in any single experiment. The regulator is of the usual pattern, although it does not involve any new principle. Any gas can be regulated in any direction by the

The stirring arrangement S, fig. 1, consists of a vertical glass tube, terminating in a horizontal T-piece open at both ends. In the vertical tube is an opening a little below the surface of the liquid. The T-tube was rotated about a vertical axis by means of a hot-air engine. The circulation of the water in the thermostat was found to be very effective when the T-piece made three revolutions a second.

(2) The wash-bottles, W, fig. 1, were each of about 100 c.c. capacity, and were all sealed together (except in some of the earlier experiments) in order to prevent leaks and the access of grease or other foreign matter. The last flask through which the air passed was connected with a pressure-gauge  $G_1$  (read by a mirror scale) by a tube with a stop-cock just above the bath.

(3) The absorption apparatus, B, fig. 1, which was connected with the tube from W by a ground-glass joint J, consisted of two small wash-flasks containing pure concentrated sulphuric acid; about 10 c.c. were placed in the first flask and 2 c.c. in the second. In the earlier experiments the two flasks were connected by rubber tube, and weighed separately, but it was found that the second never gained more than 1 mg. during an experiment, and they were therefore sealed and weighed together. As a further proof of the completeness of the absorption, in two experiments at  $80^\circ$  a tube containing phosphoric anhydride was connected up with the second bulb, but it did not increase in weight by so much as 0.1 mg.

(4) The aspirator consisted of a large bottle, H, fig. 1, placed in a large pan of water. For the experiments at the lower temperatures the bottle had a capacity of 12 litres, but for some of the higher temperature experiments a 4-litre bottle was employed. The quantity of water outside was so large that the temperature did not change more than  $0.1^\circ$  during an experiment, and hence a regulator was considered unnecessary. Water was drawn off through the tube U into graduated flasks. The pressure of the air in the bottle H was read by means of a gauge,  $G_2$ . Between the joint J and the bath, the projecting tube was surrounded by sheet brass and heated by a row of small gas jets (in the earlier experiments by a coiled wire, through which an electric current was passed), in order to prevent condensation of vapour in this part of the tube. The three-way stop-cock C was the dividing line between the flasks containing the water and the absorption apparatus; by means of it connection could be made between two U-tubes (not shown in the figure), containing strong sulphuric acid, and the absorption apparatus, so that the tube between B and C might be cleared of moisture by a current of air from the outside, passing first through the U-tubes.

Between the absorption apparatus and the aspirator were a calcium-chloride tube, Ca, and two small wash-bulbs containing water, the former to prevent water vapour from getting back to the absorption

apparatus, and the latter to saturate the air passing into the aspirator.

The weights employed were compared with a 1g. platinum weight, which had been standardised at the National Physical Laboratory. The balances employed were tested for inequality of length of arm, but in each case this was found to be negligible.

#### *Method of Work.*

An experiment was carried out as follows:—

The four wash-bottles were thoroughly cleaned by placing them in an inverted position and blowing steam through them for half an hour. This, or some similar process, is important, for if there is any grease present, erratic results are obtained. The flasks were then about two-thirds filled with distilled water, and placed in the thermostat.

The sulphuric acid was placed in the absorption apparatus, which was placed in position, and all necessary connections made. A slow stream of air was aspirated through the whole apparatus, and the two pressure gauges were read.

The absorption apparatus was weighed after standing in the balance case 15 or 20 minutes. Meanwhile the tube CJ was cleared of moisture. The absorption apparatus was then connected up again, the rubber junctions coated with wax, the pressure in the aspirator adjusted to that previously found, and the apparatus was left for some minutes to discover any possible leak. The absence of any leak being proved, the clip P and the stop-cock C were opened and the experiment begun.

To bring the experiment to an end, the clip P was first closed, and then the stop-cock C. The pressure gauge  $G_2$  was read again (it usually remained quite unaltered), and the moisture was driven from the tube CJ into the absorption apparatus (by the method already described), which was then removed to be weighed.

The temperature of the aspirator and the barometer were read during the experiment.

At the lower temperatures the air was never passed through at a greater rate than 0.1 litre per minute, while at the higher temperatures the rate was not more than 0.05 per minute. The air acquires the temperature of the bath and becomes saturated with aqueous vapour with surprising rapidity. Special experiments were made to test this point.

#### *Saturation of the Air.*

If air is passed through one wash-bottle only, containing water, and placed in a thermostat at a temperature higher than that of the air, a rapid fall of temperature takes place owing to the low temperature of the air and to the cooling by evaporation of the water. Experiments were made at 40° C. and at 76° C.; a thermometer which could be

read to  $0.01^{\circ}$  was placed in the wash-bottle through a cork in the neck, and air was drawn through at varying rates. In most of the experiments the air passed first of all through another wash-bottle containing water, and then through the flask containing the thermometer. The results are here tabulated :—

| Temperature<br>of<br>thermostat. | Wash-<br>bottle. | Air current.     | Fall of<br>temperature.   |
|----------------------------------|------------------|------------------|---------------------------|
| $40^{\circ}$ C.                  | 1                | 0.16 l. per min. | $0.12^{\circ}$ in 5 mins. |
| 40                               | 1                | 3.0    "         | $0.82^{\circ}$ "          |
| 40                               | 2                | 0.6    "         | No fall.                  |
| 40                               | 2                | 3.0    "         | "                         |
| 76                               | 2                | 0.05   "         | "                         |
| 76                               | 2                | 0.08   "         | "                         |
| 76                               | 2                | 0.14   "         | "                         |
| 76                               | 2                | 0.50   "         | Slow fall.                |
| 76                               | 2                | 0.86   "         | Rapid fall.               |

It will be noted that at  $40^{\circ}$ , with only two flasks, no perceptible fall of temperature is produced by such a rapid current of air as 3 litres per minute, while at  $76^{\circ}$ , with the same number of flasks, a current of 0.14 litre per minute has no perceptible effect. Since the rates used in the actual experiments for the determination of vapour pressure were much less than 0.14 litre per minute, and four flasks (in some cases five) were employed, there can be no doubt as to the saturation of the air in these experiments.

This was confirmed also by varying the rate during the experiments, when the variation was not found to have any effect on the amount of water driven off.

#### *Method of Calculation.*

An experiment carried out in the manner described furnishes the following data :—

W = Weight of water drawn off.

P = Pressure in the last aspiration flask.

T = Absolute temperature of air in aspirator.

V = Volume of air drawn through the water, measured at temperature and pressure of aspirator.

p = Pressure of air in aspirator.

If we assume that the vapour pressure of water is the same in the presence of air as in the absence of air or any other gas, and that the partial pressure of each constituent of the gaseous mixture is the same as if each occupied the whole space (Dalton's laws), and also that the density of saturated water vapour is normal, then the vapour pressure can be calculated from the relation

$$\frac{\text{Pressure of aqueous vapour}}{\text{Total pressure}} = \frac{\text{Volume of aqueous vapour}}{\text{Total volume}}.$$

The "normal" value of the density of aqueous vapour is taken to be that calculated from the density of oxygen\* and the molecular weight of water, and the corresponding specific volume, which is more convenient for purposes of calculation, is 1.242. The vapour pressure is calculated then from the expression—

$$\frac{1.242 \times 760 \text{ W.P.T}}{T(1.242 \times 760W) + 273.V.p}.$$

### Results.

The lowest temperature at which the method was applied was 20° C. The experiments are naturally very tedious at low temperatures owing to the large volume of air which must be passed through the apparatus. The whole of the experimental results are here tabulated, the actual data being given in an Appendix.

It will be noted that the temperatures are at exactly every 1° C (with two exceptions); the corrections were calculated beforehand and the thermostat carefully adjusted. One exception is 80.10°, which was the temperature in the only series of experiments made with a portion of the thermometer stem outside the bath; a correction was made for this exposed portion in the usual way. On calculating out the results, the vapour pressure appeared to be abnormally high, and consequently a large number of experiments were made to ascertain this point with certainty. However, on proceeding to 90°, normal vapour pressures were again obtained, and suspicions were aroused as to the exactness of the temperature reading at 80°. The thermostat was brought again to 80°, and the thermometer placed first with its stem surrounded by the wide tube and hot liquid, and then placed in the original position, when it was found that the correction had been overestimated by 0.1°. The reason for this large difference between the calculated and the real correction is probably that in this class C thermometer the column of mercury projecting from the thermostat is surrounded by a bath of hot air enclosed by the outer tube of the thermometer. The other exception, at 40.66°, was one of the earliest experiments carried out.

The vapour pressures given in the last column are taken from Ostwald and Luther's 'Physiko-chemische Messungen' (1902) p. 156. The numbers were obtained by plotting the differences between the results of Wiebe (76° to 100°) and Thiesen and Schae (-10° to +25°), and the Regnault-Broch numbers, interpolating the curve from 25° to 76°, reading off the corrections from the smoothed curve, and applying them to the Regnault-Broch numbers throughout.

\* The weight of a litre of oxygen has been taken as 1.4295 g.

| Temperature. | Vapour-pressure.<br>mm. | Mean<br>vapour-pressure. | Vapour-pressure.<br>Regnault corrected. |
|--------------|-------------------------|--------------------------|-----------------------------------------|
| 20° C.       | 17·61                   |                          |                                         |
|              | 17·69                   | mm.                      | mm.                                     |
|              | 17·53                   | 17·61                    | 17·52                                   |
|              | 17·62                   |                          |                                         |
| 30           | 31·89                   |                          |                                         |
|              | 31·81                   |                          |                                         |
|              | 32·05                   | 31·88                    | 31·73                                   |
|              | 31·79                   |                          |                                         |
| 40·66        | 57·45                   |                          |                                         |
|              | 57·36                   |                          |                                         |
|              | 57·34                   | 57·34                    | 57·15                                   |
|              | 57·33                   |                          |                                         |
|              | 57·23                   |                          |                                         |
| 50           | 92·34                   |                          |                                         |
|              | 92·33                   |                          |                                         |
|              | 92·38                   | 92·39                    | 92·35                                   |
|              | 92·50                   |                          |                                         |
| 60           | 148·8                   |                          |                                         |
|              | 149·1                   |                          |                                         |
|              | 148·5                   | 148·94                   | 149·3                                   |
|              | 149·2                   |                          | (Regnault uncorr.)                      |
|              | 149·1                   |                          | 148·9                                   |
| 70           | 234·2                   |                          |                                         |
|              | 233·2                   |                          |                                         |
|              | 234·5                   |                          |                                         |
|              | 235·0                   | 233·98                   | 234·0                                   |
|              | 233·5                   |                          |                                         |
|              | 233·5                   |                          |                                         |
| 80·10        | 358·1                   |                          |                                         |
|              | 356·6                   |                          |                                         |
|              | 358·4                   |                          |                                         |
|              | 357·4                   |                          |                                         |
|              | 357·9                   | 357·1                    | 356·9                                   |
|              | 355·0                   |                          |                                         |
|              | 357·1                   |                          |                                         |
|              | 357·6                   |                          |                                         |
|              | 356·1                   |                          |                                         |
| 90           | 526·4                   |                          |                                         |
|              | 525·6                   |                          |                                         |
|              | 527·6                   | 526·3                    | 525·8                                   |
|              | 525·7                   |                          |                                         |



It must be here remarked that the experiments at the lower temperatures are by no means so reliable as those at the higher temperatures, for the following reasons:—

(1) They were the first carried out, before experience in working the experiment had been gained.

(2) The amount of water carried over was always very small, so that it is impossible for these experiments to be so accurate as those in which the water is carried off more rapidly.

(3) A rubber connection was used at J (fig. 1), whereas in the later experiments this was replaced by a ground-glass joint. Also, the absorption flasks were weighed with glass stoppers connected by rubber tubes, and it was found that moisture from the air found its way slowly through the rubber, although the glass tubes were made to touch. The absorption apparatus was in this way found to take up sometimes as much as 0.5 mg. in an hour, which is quite sufficient to account for the highness of the numbers obtained in these experiments. This may be, perhaps, included under reason (1).

At the higher temperatures there was no rubber connection through which moisture could pass to the absorption apparatus, and the apparatus was closed with small rubber stoppers inserted into the tubes. With this arrangement the weight was found to be constant.

#### *Deductions from Experimental Results.*

The vapour pressures obtained are seen to agree very closely with those obtained by direct measurement. Now, in the calculation, certain assumptions have been made, viz., Dalton's law of partial pressures, and that the density of aqueous vapour is normal. It would thus seem that these assumptions are justified. It is highly improbable that deviations from Dalton's law, and from the normal density, should so balance one another at all these temperatures as to give correct vapour pressures. Fortunately there is independent evidence of the validity of Dalton's law under the conditions of the experiments. Galitzine,\* by some well-devised experiments, showed that there was no appreciable deviation from Dalton's law for air and aqueous vapour at moderate pressures below 100° C.

It may be concluded, then, that the density of saturated water vapour at the pressures and temperatures employed is very near the normal value. This conclusion seems to the author quite justified by the experiments described, although it is at variance with the work of a number of other investigators, who have found the density to be greater than normal, usually from 1 to 2 per cent., sometimes much more.

\* 'Wied. Ann.,' 1890, vol. 41, p. 588

A list of papers on the subject is here given for reference:—

Regnault ('Ann. Chim. Phys.' (3), 15, 129, 1845).

Fairbairn and Tate ('Phil. Trans.,' vol. 150, p. 185, 1860).

Wüllner and Grottrian ('Wied. Ann.,' vol. 11, p. 544, 1880).

Perot ('Comptes Rendus,' vol. 102, p. 1369, 1886).

Batelli ('Mem. dell' Accad. di Torino,' (2), vol. 41, p. 33, 1891, and (2), vol. 43, p. 1, 1892).

Ramsay and Young ('Phil. Trans.,' A, 1892, p. 107).

Bauer ('Wied. Ann.,' vol. 55, p. 184, 1895).

Griffiths\* has calculated the density of saturated water-vapour from latent heat of evaporation by means of the thermo-dynamical equation

$$L = \frac{T}{J} (s' - s) \frac{dp}{dT}.$$

The values of  $dp/dT$  were taken from Broch's reduction of Regnault's experimental results; the author has recalculated the densities, replacing these values of  $dp/dT$  by numbers calculated from the vapour pressures given by Luther.† Both series are given in the following table:—

| Temperature. | Regnault. | Density. | Regnault corrected. | Density.    |
|--------------|-----------|----------|---------------------|-------------|
| 0°           | 0·330     | 0·6184   | 0·340               | 0·6002      |
| 20           | 1·073     | 0·6215   | 1·031               | 0·6169      |
| 40           | 2·936     | 0·6270   | 2·942               | 0·6257      |
| 60           | 6·922     | 0·6298   | 6·927               | 0·6293      |
| 80           | 14·388    | 0·6305   | 14·35               | 0·6323      |
| 100          | 26·981    | 0·6299   | 27·20               | 0·6248      |
|              |           |          |                     | Mean 0·6215 |

This method is a very indirect one, but is free from the errors involved in most of the experimental methods. Since  $L$  and  $J$  have been determined with great accuracy, the densities calculated from them should be accurate at the higher temperatures where  $dp/dT$  is known with fair accuracy. The mean density so obtained is very close to the normal density, 0·6227.

I believe the greater number of the experiments quoted are rendered inaccurate by the condensation of vapour on the sides of the glass vessel employed, owing to the hygroscopic nature of glass; this is impossible to avoid, but in my experiments it will have

\* 'Phil. Trans.,' A, vol. 186, 1895, p. 325.

† 'Physiko-chemische Messungen,' Ostwald-Luther, p. 156.

no effect on the result, and I believe it can be safely concluded from these experiments that the density of saturated water vapour under the conditions of the experiment (that is, when mixed with half its volume to forty times its volume of air, at temperatures from 90° to 20°) is normal.

Also, it is highly improbable that the density of the saturated vapour alone is more than slightly above normal at these temperatures, as the deviations from Dalton's law have been shown to be very small. This is also confirmed by the results of Griffiths (*vide supra*).

*Summary and Conclusion.*

(1) When air is aspirated through water, it becomes saturated with aqueous vapour with great rapidity.

(2) In the saturated air so obtained, the pressure of the aqueous vapour is the same as the vapour pressure of water when no other gas is present.

(3) The density of the aqueous vapour in the mixture is normal.

(4) The density of saturated aqueous vapour (without admixture) is probably only very slightly (if at all) above normal at temperatures up to 90°.

APPENDIX.  
*Experimental Data.*

| Temperature<br>of water. | W.       | P.    | T.    | V.      | p.    | Vapour<br>pressure. |
|--------------------------|----------|-------|-------|---------|-------|---------------------|
|                          | grammes. | mm.   | C°.   | litres. | mm.   |                     |
| 20° C. ....              | 0·1744   | 735·7 | 290·8 | 10      | 715·2 | 17·61               |
|                          | 0·1752   | 740·6 | 291·0 | 10      | 720·1 | 17·69               |
|                          | 0·1735   | 739·7 | 291·0 | 10      | 719·2 | 17·53               |
|                          | 0·1746   | 735·0 | 291·0 | 10      | 715·0 | 17·62               |
| 30        .....          | 0·3213   | 739·4 | 291·0 | 10      | 717·3 | 31·89               |
|                          | 0·3215   | 740·4 | 291·1 | 10      | 718·2 | 31·81               |
|                          | 0·3225   | 737·4 | 291·3 | 10      | 714·8 | 32·05               |
|                          | 0·3134   | 743·9 | 292·0 | 10      | 722·3 | 31·79               |
| 40·66       .....        | 0·3030   | 745·3 | 289·5 | 5       | 726·4 | 57·45               |
|                          | 0·3075   | 739·0 | 286·2 | 5       | 723·0 | 57·36               |
|                          | 0·3033   | 732·7 | 289·1 | 5       | 714·1 | 57·34               |
|                          | 0·3021   | 736·8 | 289·8 | 5       | 717·1 | 57·33               |
|                          | 0·3013   | 737·5 | 290·1 | 5       | 718·0 | 57·23               |
| 50        .....          | 0·5104   | 737·9 | 290·7 | 5       | 717·3 | 92·34               |
|                          | 0·5095   | 737·7 | 291·0 | 5       | 716·8 | 92·33               |
|                          | 0·5108   | 737·5 | 290·5 | 5       | 716·8 | 92·38               |
|                          | 0·5114   | 737·5 | 290·8 | 5       | 716·6 | 92·50               |
| 60        .....          | 0·8866   | 738·4 | 294·3 | 5       | 715·1 | 148·8               |
|                          | 0·8893   | 739·5 | 294·3 | 5       | 716·2 | 149·1               |
|                          | 0·8820   | 738·5 | 295·0 | 5       | 714·4 | 143·5               |
|                          | 0·8921   | 738·0 | 294·2 | 5       | 715·8 | 149·2               |
|                          | 0·9032   | 739·7 | 291·0 | 5       | 720·2 | 149·1               |
| 70        .....          | 0·6802   | 745·9 | 285·0 | 2·005   | 730·1 | 234·2               |
|                          | 0·5878   | 745·2 | 285·3 | 1·747   | 728·4 | 233·2               |
|                          | 0·6768   | 750·4 | 285·3 | 2·005   | 732·6 | 234·5               |
|                          | 0·6785   | 750·4 | 285·5 | 2·005   | 732·4 | 235·0               |
|                          | 0·6610   | 761·7 | 287·8 | 2·005   | 742·1 | 233·5               |
|                          | 0·6616   | 760·9 | 287·9 | 2·005   | 742·0 | 233·5               |
| 80·10       .....        | 1·3616   | 754·1 | 284·8 | 2·004   | 739·5 | 358·1               |
|                          | 1·3626   | 735·1 | 287·4 | 2·004   | 717·3 | 356·6               |
|                          | 1·3870   | 729·2 | 287·4 | 2·004   | 711·4 | 358·4               |
|                          | 1·3987   | 728·2 | 286·4 | 2·004   | 711·7 | 357·4               |
|                          | 1·3642   | 746·7 | 295·6 | 2·020   | 730·3 | 357·9               |
|                          | 0·6672   | 752·9 | 285·8 | 1·003   | 736·7 | 355·0               |
|                          | 1·3526   | 753·2 | 284·9 | 2·004   | 737·3 | 357·1               |
|                          | 1·3502   | 754·3 | 285·7 | 2·004   | 738·2 | 357·6               |
|                          | 1·3413   | 753·3 | 285·7 | 2·004   | 737·2 | 356·1               |
| 90        .....          | 3·4143   | 756·9 | 286·7 | 2·004   | 739·3 | 526·4               |
|                          | 3·4420   | 755·5 | 284·9 | 2·004   | 739·6 | 525·6               |
|                          | 3·4635   | 753·1 | 286·6 | 2·004   | 735·9 | 527·6               |
|                          | 3·4036   | 756·1 | 287·0 | 2·004   | 738·6 | 525·7               |

"The Spectra of Neon, Krypton, and Xenon." By E. C. C. BALY,  
Lecturer on Spectroscopy in University College, London.  
Communicated by Sir WILLIAM RAMSAY, K.C.B., F.R.S.  
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(Abstract.)

The gases were illuminated by the passage of the discharge from an induction coil through them under reduced pressures. Vacuum tubes were filled with each one of them, and the glowing gas in a capillary portion was examined "end on" through a quartz window. Considerable difficulty was experienced in the use of the vacuum tubes, owing to the rapid absorption of the gas by the electrodes when the electric current was kept passing for long periods. It was found that when the gases were quite pure, and free from any diatomic impurities, the aluminium electrodes were readily volatilised, an aluminium mirror being formed upon the immediately surrounding walls of the tube; at the same time the electrodes became very hot and it was necessary to make them of very stout wire, *e.g.*, No. 12 B.W.G. Special care had to be taken in making each individual electrode so as to enable it to withstand the disintegrating action of the discharge. The unusual heating of the electrodes gave rise to considerable trouble on account of the large quantities of hydrogen evolved from them; it is a common experience to anyone, when filling a new vacuum tube, to find a quantity of hydrogen given out by the electrodes; this hydrogen, as is well known, may be readily removed by further exhaustion. If, however, into a tube from which this hydrogen has been removed a small quantity of one of the monatomic gases be introduced, a further large quantity of hydrogen is evolved from the electrodes. Every trace of this second quantity of hydrogen must be removed before the tube can be depended upon; it is necessary to thoroughly wash out the tube by repeated admission of argon and re-exhaustion.

The measurements were all made upon photographs taken with a Rowland concave grating of 10-foot radius and 14,438 lines to the inch; the first three orders of spectra were employed and nearly all the chief lines were measured in two orders. As far as can be estimated by the coincidences between the different spectra, the probable error is less than  $\pm 0.03$  Ångström unit. The spectra are all composed of bright lines and are absolutely characteristic in each case. While neon possesses only one spectrum, krypton and xenon both have two, one being given when the ordinary discharge is passed and the other when a Leyden jar and spark gap are placed in the circuit; this second spectrum is much more

complex than the first in each case, an analogy being thus shown with argon.

There are about forty lines of weak intensity common to the jar and spark gap spectra of krypton and xenon; this may possibly be considered as evidence of the existence of another element of higher atomic weight in the same series.

In the tables of the spectra, columns are given of the measurements which have appeared by Liveing and Dewar and by Runge in the case of krypton. A very satisfactory agreement is to be observed between the two series of measurements, although those of Liveing and Dewar are only given to the fourth place. It is interesting that these authors give, in their list of the spectrum lines of the most volatile gases of the atmosphere, about 162 lines which do not appear on the neon photographs, and, therefore, in all probability, do not belong to this gas.

The most important lines in the visible region of the spectrum are given in the following tables:—

#### Neon Spectrum.

| Wave-lengths. | Intensity. | Wave-lengths. | Intensity. |
|---------------|------------|---------------|------------|
| 6402·40       | 10         | 6096·37       | 10         |
| 6383·15       | 8          | 6074·52       | 10         |
| 6328·38       | 6          | 6030·20       | 10         |
| 6304·99       | 8          | 5975·78       | 8          |
| 6266·66       | 10         | 5974·73       | 6          |
| 6217·50       | 8          | 5944·91       | 10         |
| 6182·37       | 10         | 5882·04       | 8          |
| 6163·79       | 10         | 5852·65       | 20         |
| 6143·28       | 10         | 5764·54       | 8          |
| 6128·63       | 8          | 4259·53       | 6          |

#### The First Krypton Spectrum.

| Wave-lengths. | Intensity. | Wave-lengths. | Intensity. |
|---------------|------------|---------------|------------|
| 5871·12       | 10         | 4454·12       | 10         |
| 5570·50*      | 10         | 4400·11       | 6          |
| 5562·45       | 6          | 4376·33       | 10         |
| 4671·40       | 10         | 4362·83       | 9          |
| 4624·48       | 10         | 4319·76       | 10         |
| 4502·56       | 9          | 4318·74       | 8          |
| 4501·13       | 7          | 4274·15       | 10         |
| 4463·88       | 10         |               |            |

\* Probably the green Aurora line.

## The Second Krypton Spectrum.

| Wave-lengths. | Intensity. | Wave-lengths. | Intensity. |
|---------------|------------|---------------|------------|
| 5633·17       | 6          | 4109·38       | 6          |
| 4765·90       | 6          | 4098·89       | 7          |
| 4762·60       | 5          | 4088·48       | 8          |
| 4739·16       | 7          | 4067·53       | 5          |
| 4659·04       | 5          | 4065·22       | 8          |
| 4634·05       | 5          | 4057·17       | 8          |
| 4619·31       | 6          | 4050·62       | 5          |
| 4615·46       | 5          | 4044·80       | 5          |
| 4577·40       | 6          | 3998·10       | 5          |
| 4523·32       | 5          | 3994·98       | 6          |
| 4475·18       | 7          | 3954·90       | 5          |
| 4355·67       | 10         | 3920·29       | 8          |
| 4317·98       | 5          | 3917·76       | 6          |
| 4300·67       | 5          | 3912·69       | 5          |
| 4293·10       | 6          | 3906·37       | 8          |
| 4145·28       | 6          |               |            |

## The First Xenon Spectrum.

| Wave-lengths. | Intensity. | Wave-lengths. | Intensity. |
|---------------|------------|---------------|------------|
| 4923·28       | 6          | 4524·83       | 6          |
| 4916·63       | 6          | 4501·13       | 10         |
| 4807·19       | 6          | 4193·70       | 8          |
| 4734·30       | 8          | 4116·25       | 7          |
| 4697·17       | 7          | 4109·84       | 5          |
| 4671·42       | 10         | 4078·94       | 10         |
| 4624·46       | 15         | 3967·74       | 10         |
| 4582·89       | 5          | 3951·16       | 10         |

## The Second Xenon Spectrum.

| Wave-lengths. | Intensity. | Wave-lengths. | Intensity. |
|---------------|------------|---------------|------------|
| 6097·80       | 7          | 5460·63       | 6          |
| 6051·36       | 7          | 5450·71       | 5          |
| 6036·40       | 6          | 5439·19       | 8          |
| 5976·67       | 7          | 5419·40       | 10         |
| 5751·28       | 5          | 5372·62       | 8          |
| 5727·15       | 5          | 5339·56       | 9          |
| 5719·83       | 6          | 5314·15       | 8          |
| 5667·85       | 6          | 5292·40       | 10         |
| 5659·67       | 5          | 5262·16       | 5          |
| 5616·99       | 6          | 5260·65       | 5          |
| 5531·33       | 7          | 5191·60       | 5          |
| 5472·90       | 7          | 5080·88       | 7          |

| Wave-lengths. | Intensity. | Wave-lengths. | Intensity. |
|---------------|------------|---------------|------------|
| 4921·68       | 6          | 4415·00       | 7          |
| 4890·24       | 5          | 4406·99       | 5          |
| 4887·47       | 5          | 4395·91       | 10         |
| 4883·68       | 6          | 4393·34       | 10         |
| 4876·68       | 7          | 4330·63       | 15         |
| 4862·69       | 8          | 4296·52       | 5          |
| 4844·50       | 10         | 4245·54       | 10         |
| 4823·47       | 6          | 4238·37       | 10         |
| 4698·20       | 5          | 4223·14       | 5          |
| 4683·76       | 5          | 4215·77       | 5          |
| 4652·15       | 6          | 4214·17       | 5          |
| 4615·72       | 5          | 4213·80       | 5          |
| 4603·21       | 10         | 4208·61       | 6          |
| 4592·22       | 6          | 4193·25       | 8          |
| 4585·65       | 10         | 4180·20       | 10         |
| 4577·36       | 6          | 4158·14       | 5          |
| 4545·34       | 8          | 4145·85       | 5          |
| 4541·03       | 8          | 4109·20       | 6          |
| 4532·67       | 5          | 4057·55       | 5          |
| 4524·38       | 5          | 4050·19       | 6          |
| 4481·01       | 7          | 3992·98       | 5          |
| 4462·38       | 20         | 3950·70       | 8          |
| 4448·28       | 10         | 3922·67       | 10         |
| 4434·35       | 6          | 3908·00       | 7          |

he total numbers of lines measured in the five spectra are as  
ws:—

|                  |            |
|------------------|------------|
| Neon .....       | 164 lines. |
| Krypton I .....  | 74 „       |
| Krypton II ..... | 700 „      |
| Xenon I .....    | 92 „       |
| Xenon II .....   | 1370 „     |

ere are, 17 lines which are common to the two Krypton Spectra,  
7 common to those of Xenon.



"On a Remarkable Effect produced by the Momentary Relief of Great Pressure." By J. Y. BUCHANAN, F.R.S. Received May 14,—Read May 28, 1903.

[PLATES 1 AND 2.]

The effect is shown in the brass tube and the copper sphere which I have the honour to exhibit to the Society. It is also illustrated in figures 1—4 which accompany this paper.

The experiment was made for the first time on board the "Challenger" in the early part of the cruise. At that time the deep sea thermometers, with protected bulb, had only been recently introduced, and the effect of pressure on thermometer bulbs, whether protected or not, occupied public attention. In the deepest sounding made by the "Challenger" in the Atlantic, namely, that of March 26, 1873, when a depth of 3875 fathoms was reached, both the thermometers, which were sent to the bottom, collapsed. It, therefore, became a question what recommendation should be made to the thermometer makers to assist them in producing thermometers which shall be able to withstand the greatest pressure to which they are likely to be exposed in the work of ocean sounding.

For this purpose I immediately prepared the following experiment:—I took glass tubes of three different calibres. The widest had about the calibre of the outer bulb of a *Millar-Casella* thermometer, the narrowest had an internal diameter of 6 mm., and the third had a diameter of about 10 mm. A length of 75 mm. of each was sealed up at both ends, and the three tubes were wrapped in a cloth and enclosed in the cylindrical copper case of a deep-sea thermometer.

The upper and lower ends of these cases are pierced with many holes in order to permit the passage of water through them. On the next day, March 27, 1873, the case was attached to the sounding line and a depth of about 2800 fathoms was reached. When the case came up again it looked as if someone had struck it in the middle with a hammer. When it was opened and the cloth unfolded, it seemed for a moment as if it were full of snow, but a second look showed that what appeared to be snow was nothing but finely comminuted glass. The two wider tubes had collapsed, but the narrow one was intact. At first sight the effect produced on the copper case was puzzling, but after a little study and reflection its nature became apparent.

No account of the experiment has been published, and when I was able, through the kindness of H.S.H. the Prince of Monaco, to join his yacht the "*Princesse Alice*" for her cruise of last summer, I determined to repeat it, and, if possible, to vary it. Owing to press of

other work, nothing was done until near the end of the cruise. The brass tube (figs. 1 and 2, Plate 1) above referred to, was the case for holding a piezometer which was accidentally broken. With it I repeated the experiment which I had made in the "Challenger," with this difference, that I used only one sealed glass tube. It was an ordinary pipette of 50 c.c., sealed up at both ends close to the body. It was wrapped in a piece of muslin and loosely packed with cotton waste so as to occupy the middle of the brass tube.

The length of the brass tube was 33 cm., and its diameter 4.13 cm. Its weight without the cover was 350 grammes. Both the top and the bottom are pierced with many holes so as to allow passage to the water.

Thus charged, it descended on the sounding line to a depth of 3000 metres, and when it came up it was evident from its appearance that the experiment had succeeded. As in the experiment on board the "Challenger," the glass tube had been converted into a snow-white powder. The external effect also was confined entirely to that part of the brass tube which had been occupied by the sealed glass tube. Above and below it there was no disfiguration.

The copper ball (figs. 3 and 4, Plate 2) is an ordinary 5-inch ball for the supply tap of a cistern. A spherical glass fractionating flask, having a diameter rather less than  $1\frac{1}{2}$  inch, was hermetically sealed close to the spherical body. It was then wrapped in a piece of muslin, and with loose packing of cotton waste it was enclosed between the two copper hemispheres, which were then soldered together. The holes at the poles of the copper sphere gave free communication with the sea water. The copper ball was then attached to the dredging cable, which took it to a depth of 3000 metres. When it came up no external effect was visible. I could not believe that even a small flask of the kind could support a pressure of 300 atmospheres, and I concluded that it had collapsed shortly after leaving the surface. Still, as the line was going to make a second excursion, and this time to 6000 metres, I re-attached the ball along with a larger one to it.

On returning to the surface the ball had the appearance which you see. If the soldered welt represent the equator, it will be seen that both polar areas are as they were. Perpendicularly to the equator a system of folds or creases runs northwards and southwards and extends very little beyond the tropics. The creasing is most accentuated at a part of the equator where there is a slight flattening. It is evident that the glass flask when it collapsed was relatively near this part of the ball. I did not open the ball, as I thought it would be more instructive to keep it as it is. The débris of the glass flask with the cotton waste is still inside it.

The effect of the sudden relief of pressure on the copper ball is

distributed much more uniformly over it than is the case in the brass tube. In the latter the effect is very powerful and very local. In both cases the effects which we see have been produced in a moment of time, and are properly speaking, the effects of violent shock. It is remarkable that in the ball the equatorial zone which has the welt to stiffen it should be the field of all the disfigurement, while the polar areas which have no strengthening have not been exposed, or at least have not yielded to strain.

If we examine the brass tube, figs. 1, 2, we see that, with the exception of the portion nearly in the middle which held the sealed glass tube, the case has perfectly preserved its cylindrical form. The distortion or crumpling affects only the part where the tube collapsed, and it is evident that it did not occupy a truly axial position, but lay nearer that part of the brass envelope where the ears for attachment to the sounding line are situated. Here a most formidable corrugation (fig. 1) has been produced, the metal being pinched into a fold so as almost to meet inside. Besides this, there are two minor corrugations. A greater thickness of water intervened between this part of the brass envelope and the enclosed glass tube, and the small effect produced shows that the difference of pressure within and without the brass tube was here comparatively small. It will be observed that the butt-joint of the tube has been opened at fig. 2; but this is a secondary effect due to the distortion.

The brass tube, as it stands, is a manometer or pressure gauge which records the distribution of pressure in it while filled with and immersed in water, during the instant of time when, while the pressure on all sides is very great, the pressure at a locality in the interior suddenly becomes nothing or very small. The effect of this sudden difference of pressure has been concentrated on the part of the brass tube nearest to which the glass tube was situated. Here the diminution of internal volume of the brass tube produced by the principal corrugation must, from rough measurements, be very nearly equal to that of the glass tube which collapsed. At first sight it appears remarkable that on the collapse of the glass tube, when it was free to the compressed sea water to fill up the void with water through the two open ends, instead of doing so, it filled it by pinching up the stout brass of which the tube was made, to such an extent as to obliterate the void.

The experiment shows us that it was easier in the time to pinch the envelope of brass than to shove in the plugs of water at both ends. The complete absence of distortion or disfigurement of the upper and lower portions of the brass tube shows that the tension of the water in these two portions of the tube was not materially diminished in the time between the collapse of the glass tube and the occupation of its place by the corrugation of the envelope. In considering this experiment, we must distinguish between the tension and the pressure of the

water. When the water is at rest they are equal. During a catastrophe of this kind the balance is destroyed, as in the case of air which is transmitting a sound wave. If water were incompressible, it could have no tension, however great the pressure to which it might be exposed. What pinched the brass tube was not the column of 2000 or 3000 metres subsiding on it, but the resilience of the unlimited supply of water in its neighbourhood at the high tension due to its compression by a pressure of 200 or 300 atmospheres. Relatively, this acts instantaneously; while, to put in motion a mass of water takes a definite time. The quantity of water contained in the brass tube is not sufficient for its resilience to produce any counter-vailing effect to the resilience of the mass of compressed sea water outside.

In the case of the copper sphere it is otherwise. Its diameter is 5 inches, that of the sealed glass bulb inside of it was between 1 and  $1\frac{1}{2}$  inch, and certainly not greater than  $1\frac{1}{2}$  inch. If we assume it to have been  $1\frac{1}{2}$  inch, then its volume is to that of the copper sphere in the proportion  $3^3 : 10^3 = 27 : 1000$ . If we assume that the glass bulb succumbed at a depth of 5000 metres, or at a pressure of 500 atmospheres, then the resilience of the water inside of the copper sphere would have a very considerable effect in neutralising the crushing action of the water outside. At the low temperature found at great depths in the ocean the volume of a mass of distilled water is compressed by 2.5 per cent. by a pressure of 500 atmospheres. The compressibility of sea water is nine-tenths of that of distilled water, therefore, it would be compressed by 2.25 per cent. The compression produced by a pressure of 500 atmospheres is equal to the expansion when the pressure is diminished by the same amount. But the volume of the glass bulb was not greater than 2.7 per cent. of that of the copper sphere, and it was probably less; therefore the water in the copper sphere would, at the moment of the collapse of the glass sphere, expand by very nearly the volume of the collapsed bulb, and the copper ball would then be filled, at the moment, with water having a tension equal to about atmospheric pressure. Its tension would then be brought up to 500 atmospheres by the entry of water through the holes at the two poles. The expansion of the mass of compressed water in the copper sphere takes off from the suddenness of the action, while it at the same time reduces, by at least one-half, the difference of pressures outside and inside the sphere at the instant of collapse, and this is the agent which reforms the metal sphere.

By altering the relation between the volume of the copper sphere and that of the glass sphere enclosed in it and the pressure to which the system is exposed, the effect produced may be varied at will. When experimenting in the sea, the volume of the compressed water outside of the copper sphere is practically infinite. If it is sought to reproduce these effects in the laboratory, then a very large pressure

vessel must be used. If a pressure vessel of limited size be used, altering the experiment, if the hermetically sealed glass sphere and copper sphere with its polar perforations be placed in it separately, then when the pressure is raised to such a point that the glass sphere collapses, the copper sphere will burst outwards.

I was profoundly impressed at the time by the experiments which were made on board the "Challenger," and I connected them with another experiment which is familiar to chemists. When substances are so react upon one another in a sealed tube, there is frequently disengagement of gas which produces a very high tension in the interior of the tube even when cold. If it is sought to open the tube by breaking the sealed point, an explosion is almost sure to take place. This has very serious consequences, and yet it has been produced by the relief of pressure. These examples of the destructive effect which can be produced by the sudden relief of pressure led me to believe that many shocks of earthquake may be due to similar relief of subterranean pressure.

These experiments, whether made with the copper ball or with the brass tube, furnish striking demonstrations of the importance of the element of *time* in all physical considerations.

The collapse of the brass tube, under the peculiar circumstance of the experiment, is the exact counterpart of the experiment which is frequently, but unintentionally, made by people out shooting, especially in winter. If, from inattention or other cause, the muzzle of the gun gets stopped with a plug of even the lightest snow, the gun, if filled with this plug in its muzzle, invariably bursts. Light as the plug of snow is, it requires a definite time for a finite pressure, however great, to get it under way. During this short time the tension of the powder gases becomes so great that the barrel of the ordinary fowling-piece is unable to withstand it and it bursts.

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*Fig. 1.*



*Fig. 2.*





**Fig. 3.**



**Fig. 4.**





"The Bionomics of *Convoluta Roscoffensis*, with special Reference to its Green Cells." By F. W. GAMBLE, D.Sc., Owens College, Manchester, and FREDERICK KEEBLE, M.A., University College, Reading. Communicated by Professor S. J. HICKSON, F.R.S. Received April 24,—Read June 18, 1903.

The communication is an abstract of our observations on the Bionomics of *Convoluta Roscoffensis*, the green Turbellarian peculiar to the coast of Brittany.

A detailed illustrated account of these observations will be published shortly. The work was begun at Roscoff in 1901, and has been carried on since at Trégastel (Côtes du Nord), and in the laboratories of Owens College, Manchester, and University College, Reading. It contains the following sections:—

1. Food; 2, Development of the Green Cells; 3, Tropisms; 4, Ecology.

#### I.—Food.

*A. Previous Observations.*—Previous observers have failed to demonstrate the presence of ingested solid food in either the larval or adult stage of *Convoluta*. Geddes,<sup>1</sup> Von Graff,<sup>2</sup> and Haberlandt,<sup>3</sup> concluded that *Convoluta* does not feed, but that the animal derives its food-material from the products of the photosynthesis carried on by its green cells.

Geddes and Haberlandt were confirmed in this conclusion on finding that the animal, when placed in darkness, dies in the course of two or three days.

*B. Observations by the Authors.*—Our observations stand in direct contradiction to these. *Convoluta* feeds, and feeds voraciously. From the time of hatching up till the time of commencing maturity, *Convoluta* (1–5 mm. long) ingests diatoms, algæ, spores, grains of sand and colonies of bacteria. It also takes up such substances as litmus, congo-red, &c., with avidity. Mature and immature specimens digest masses of their own green cells, the discoloured remains of which form conspicuous brown clumps in the gut.

Moreover, we have maintained *Convoluta* alive in complete darkness for more than a fortnight, and find that the starch of the green cells disappears with extreme slowness: not till after five days of darkness in young (1–2 mm. long) animals; seven days in adults.

We conclude:—

- (1) that *Convoluta* has not lost its power of independent nutrition.
- (2) That the animal obtains little, if any, food from the reserves of its green cells.
- (3) That the sand in which *Convoluta* lives is not barren of other life as Von Graff supposed, but that it supports a rich and varied flora and fauna.

We have demonstrated the dependence of starch formation in the green cells on the presence of light, by maintaining animals in darkness till all reserve-starch has disappeared and then exposing them to light. Starch makes its appearance in the green cells after less than ten minutes exposure to bright sunlight.

By the use of monochromatic screens, we show that the rays which are most active are—as in plant chloroplasts—those between B and C (Fraunhofer lines); that no assimilation (as measured by reserve starch) takes place in the green; that some occurs in the blue. The spectrum of the alcoholic extract of chlorophyll of *Convolvula* examined by the hand spectroscope shows the chief absorption band of chlorophyll (between B and C) and strong absorption of the blue end.

## II.—Development of the Green Cells.

A. *General*.—Direct proof that the green or yellow cells of protozoa, Coelenterates, Turbellaria and other animals are due to an infection from without has been obtained only in the cases of sea anemones (Brandt<sup>4</sup>), *Hydra viridis* and *Stentor* (Beyerinck<sup>5</sup> and Famintzin<sup>6</sup>). The pure cultures, in the latter cases, have been identified with the green alga, *Chlorella vulgaris*. A similar origin by infection is assumed for the green cells of other animals, and the relation is generally regarded in all cases as a symbiosis.

B. *Previous Observations*.—With respect to *Convolvula*, Haberlandt failed to cultivate the green cells. Observing their remarkable histological features (absence of cellulose wall, &c.), he put forward the hypothesis that the green cells are now parts of the animal—animal cells to which a leucoplast is transmitted from the egg.

Georgévitch<sup>7</sup> hatched out *Convolvula*, showed that it develops as a colourless larva, and claims that such a colourless larva, if kept in sterilised water, fails to develop green cells and dies within two days. He concluded that the green cells gain access to the animal from the sea-water.

C. *Experiments of the Authors*.—Our experiments lead us to the following conclusions:—

- a. A leucoplast cannot be detected in the egg.
- b. *Convolvula*, hatched in sterilised water, may live for two weeks therein.
- c. The first indication of the future green cell is colourless and not green. Infection, if it occur, is by a colourless cell.
- d. The precautions to insure sterile conditions taken by Georgévitch and by ourselves in our earlier experiments are useless. In these experiments the egg-capsule was placed in sterilised water. We find, however, that the egg-capsule bears a rich and varied collection of green, pale green and colourless cell-colonies.

- e. Contrary to Georgévitch's statement, when hatched from egg-capsules placed in sterilised water, *Convolutas* are found, in a certain number of cases, to develop green cells. Hence either the green cells are not the result of infection, or infection may take place from the capsular flora.
- f. The latter alternative is probably correct, for the more precautions are taken to protect hatching *Convoluta* from infection, the fewer are the cases in which green cells or their colourless antecedents make their appearance in the animals.
- g. The colourless antecedents of the green cells are first seen in the gut, just above the mouth.

D. *Conclusions.*—Direct proof of infection is lacking. The evidence, however, points most strongly to infection. The infecting organism is a colourless cell. Infection often takes place from the capsule. The situation and colourlessness of the infecting cell suggest the view that this cell is a saprophytic stage in the life history of the green cell. Such saprophytic colourless stages are well known in green algae, diatoms, and flagellates (Krüger,<sup>8</sup> Karsten,<sup>9</sup> Dangeard<sup>10</sup>).

The colourless cells are taken up in company with other organisms. A pure culture is made from this mixed infection in the gut of the animal. There the cells divide and, contained in wandering cells, are carried to their final station in the periphery of the body. Some remain colourless. The majority become green.

We regard the presence of the green cells as due to a peculiar and special case of phagocytosis, in which neither green cell nor wandering cell is destroyed.

The facts do not lend support to the view that the relation between animal and alga is symbiotic.

The green cells undoubtedly derive food from the animal. The animal derives but little if any food from the green cells. We regard the green cells as facultative parasites. In their relationship to their host they recall, in some measure, such cases as *Chlorochytrium lemnae* and other green algae which live in the leaves of aquatic and other plants.

### III.—*Tropisms.*

A. *Previous Observations.*—Geddes (1879) first recorded positive phototropism (phototactism). Von Graff and Haberlandt (1891) observed negative geotropism in stillness, positive geotropism in the presence of vibrations.

B. *Observations of the Authors.*—a. *Geotropism.* The observations cited above were confirmed. The young at hatching react to gravity in the same way as adults. In the absence of the otolith, geotropism does not occur.

The reflex mechanism involves the anterior end of the body. The hinder end of animals divided transversely does not react to gravity.

*b. Thermotropism.*—*Convoluta* is attuned to a high heat-intensity. It is athermotropic at ordinary temperatures. Just below the lethal point (38° C.) it is negatively thermotropic. The response, however, is singularly and often fatally imperfect.

*c. Phototropism.*—*Convoluta* is positively phototropic, but only under certain conditions. A sudden elevation of light-intensity induces a negative phototropism. Back-ground may inhibit phototropic response.

At the moment of hatching *Convoluta* is aphototropic. The power of response to light develops rapidly, appearing a few hours after hatching.

The anterior end only of animals divided transversely is phototropic.

The rays active in producing phototropism are the green. The blue rays, which are active in inducing movement in zoospores, in *Euglena* and in plants generally (Pfeffer<sup>11</sup>), produce no tropic effect in *Convoluta*. The red rays produce a feeble negative tropism.

The tonic influence of light is more important than the tropic influence. To the former influence is due the remarkable periodic "tidal" movement which, as we have found, *Convoluta* performs. After a spell of insolation, colonies sink below the surface, and after a certain sojourn in darkness they return to the surface. These movements synchronise with the covering and uncovering of the *Convoluta* zone by the tides. They take place in colonies brought into the laboratory, but do not occur when such colonies are kept in darkness. *Convoluta*, after a certain spell of illumination, passes into a condition of light-rigor. In this condition it is singularly inert and susceptible to mechanical injury.

*d. Rheotropism.*—*Convoluta* reacts to changes in rate of flow of water. In a moderate stream, it tends to move up stream. Under the stimulus of a suddenly increased flow it sticks to the ground; when this is impossible, it contracts itself and is carried down stream.

#### IV.—Ecology.

*A. Previous Observations.*—Geddes and Von Graff have recorded the distribution of *Convoluta* along the shores of the Ile de Batz, Roscoff. They describe the rapid disappearance of the colonies when the sand is tapped or when the tide flows over them. They suggest that light and gravity provide the stimuli whereby these movements are regulated.

*B. Observations of the Authors.*—The *Convoluta* zone is determined by the outflow of drainage tidal water. The upper limit of the zone corresponds to the high-water mark of lowest neap tides. This situation insures the maximum of light-exposure consistent with security from desiccation. *Convoluta* is neither a sub-aërial nor a

marine animal. It lives in a film of water, and has migrated, from the sea, shorewards to the highest level consistent with aquatic life.

The stations occupied by *Convoluta* are remarkably constant. The constituent patches of a colony may be recognised day after day for months together. Nevertheless, diurnal and fortnightly variations in the size of the colonies occur.

The diurnal variations are tidal; each patch reaches its maximum size soon after its site is exposed. The size slowly decreases till the tide comes in. When the tide comes within a few feet, the patch disappears suddenly. At night the colonies do not ascend.

In addition to its daily variations, *Convoluta* exhibits a fortnightly lunar variation. The colonies, with their constituent patches, increase to a maximum during spring-tides, and decrease to a minimum during neap-tides.

The daily variations are due to the tonic effect of light, in which tonic effect must be included the "after-effect" of prolonged light-exposure.

The fortnightly variations are due to periodicity of reproduction. The majority of animals of a mature colony discharge their eggs in egg-capsules at the onset of the spring tides. The capsules are laid beneath the sand. In most cases the body of the animal is ruptured during the process of laying. The hinder half remains in the sand, the head end rises and joins the patch. Thus at neap-tide the size of the patches and hence of the colony is decreased.

The colonial habit of *Convoluta* which distinguishes it from its allies appears to be an indirect result of its tropisms. In obedience to tropic stimuli it becomes adept at *vertical* movements to the exclusion, in very large measure, of horizontal movements.

The lethargic state induced by prolonged light and prolonged darkness also tends to preserve groups of *Convoluta* on the patch to which they belong. Gregariousness is in this view a negative quality.

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"A Method for the Investigation of Fossils by Serial Sections."

By W. J. SOLLAS, D.Sc., LL.D., F.R.S., Professor of Geology and Palæontology in the University of Oxford. Received May 19,—Read June 11, 1903.

(Abstract.)

Mechanical difficulties preclude the study of fossils by serial thin slices, but serial polished surfaces may be obtained at any desired degree of proximity, and these, when the fossil and its matrix offer sufficient optical contrast, serve most of the purposes of thin slices. They may be photographed under the microscope, so as to furnish a trustworthy and permanent record. The sections may be used to obtain reconstructions of the fossil in wax. Several fossils have been successfully studied in this way: such as *Palæospondylus Gunni*, *Ophiura Egertoni*, *Lapworthura Miltoni*, *Monograptus priodon* and *Palæodiscus ferox*. The sections are obtained at regular intervals, usually of 0.025 mm., by means of an apparatus designed for the purpose by the Rev. F. Jervis-Smith, F.R.S., Reader of Mechanics in the University.

"An Account of the Devonian Fish, *Palæospondylus Gunni*, Traquair." By W. J. SOLLAS, D.Sc., LL.D., F.R.S., Professor of Geology and Palæontology in the University of Oxford, and IGERNA B. J. SOLLAS, B.Sc., Lecturer in Zoology, Newnham College Cambridge. Received May 19,—Read June 11, 1903.

(Abstract.)

This fossil, which has been variously referred to an alliance with Lampreys, Tadpoles, and Lung-fish, has been successfully studied by means of serial sections. The ventral surface of the head bears four pairs of branchial bars, with the last of which two post-branchial plates, the so-called "post-occipital" plates, are associated; in front of the branchial bars are two pairs of structures, which are regarded as representing the lower jaw and hyoid; they are supported by a

suspensory apparatus, which may represent the palato-quadrate and hyo-mandibular elements. The branchial arches are wholly unlike anything seen in Marsipobranchs, but call to mind the similar structures in the Dipnoi and larval Amphibians. The dorsal side of the skull shows a large cranial cavity with thin vertical walls, but no complete roof, a pair of auditory and a pair of nasal capsules. The eye was situated over a structure which resembles a sub-orbital bar, but which is sub-divided into a hyo-mandibular and palato-quadrate element. At the anterior extremity of the skull are processes which may be compared with the rostral processes of Elasmobranchs. The vertebrae are cyclo-spondylous, with large neural arches.

The organism was evidently a primitive fish, with some features which are suggestive of Marsipobranchs, some of Elasmobranchs, and some of young Dipnoi or larval Amphibians; after branching off from the Piscine stem, at a point below the origin of the Elasmobranchs, it pursued an independent course of development.

The substance of which the fossil consists is a true coal: *Coccosteus* is sometimes similarly preserved, and an analysis of the latter, kindly made by Mr. J. E. Marsh, M.A., yielded the following results:—

|                              |       |
|------------------------------|-------|
| Carbon .....                 | 68·4  |
| Hydrogen .....               | 4·5   |
| Oxygen (by difference) ..... | 11·3  |
| Ash .....                    | 15·8  |
|                              | <hr/> |
|                              | 100·0 |

Abstracting the ash, the residue closely resembles in composition an ordinary non-caking coal, such as that of South Staffordshire, as will be seen from the following table:—

|                              | Coal from<br><i>Coccosteus</i> . | Non-caking<br>Coal. |
|------------------------------|----------------------------------|---------------------|
| Carbon .....                 | 81·1                             | 79·39               |
| Hydrogen.....                | 5·3                              | 5·36                |
| Oxygen (by difference) ..... | 13·6                             | 15·25               |
|                              | <hr/>                            | <hr/>               |
|                              | 100·0                            | 100·00              |

The skeleton of *Coccosteus* also occurs in a different state of fossilisation: in this the organic matter has disappeared, leaving a mineral residue, in which the original structure is preserved, and may be recognised as that of bone. Thus definite proof is afforded of a transformation, previously suspected, by which bone may be converted into coal.



"On the Optical Activity of the Nucleic Acid of the Thymus Gland." By ARTHUR GAMGEE, M.D., LL.D., F.R.S., Emeritus Professor of Physiology in the Owens College, Victoria University, and WALTER JONES, Ph.D., Associate Professor of Physiological Chemistry in the Johns Hopkins University. Received May 15,—Read May 28, 1903.

We have lately shown\* the dextrorotatory character of the nucleoproteids of the pancreas, thymus, and suprarenal gland. We have, in the course of our investigations, shown that the "nucleins" possess a stronger rotation than the "nucleoproteids" properly so called, and from which they are derived, and in the researches which we have planned, and which naturally are suggested by our previous work, the first step appeared to us to be to determine the optical activity of the nucleic acids corresponding to the nucleoproteids investigated by us.

In the present paper we shall confine our attention to the optical activity of thymus-nucleic acid, prepared by the method of Kossel and Neumann.† We adhered closely to the method recommended by these chemists, which furnishes with great ease a colourless product, yielding colourless and perfectly transparent solutions admirably adapted for polarimetric observations. From 6 kilogrammes of trimmed thymus Kossel and Neumann obtained 120 grammes of pure nucleic acid. From 600 grammes of the gland we obtained 9·5 grammes, though no special pains were taken to work even in an approximately quantitative manner. Our purified product, like that of Kossel and Neumann, was free from proteid and barium.

1. An amount of nucleic acid weighing 1·109 grammes was suspended in water and dissolved by the cautious addition of dilute solution of ammonia in small quantities, so that when solution had been effected the reaction of the solution towards litmus was neutral. The volume of the solution was made up to 100 c.c. and it was then examined polarimetrically.

|                                   |                |
|-----------------------------------|----------------|
| Weight of substance (W).....      | 1·109 grammes. |
| Volume of solution (V) .....      | 100 c.c.       |
| Length of tube (L) .....          | 200 m.m.       |
| Observed angle ( $\alpha$ ) ..... | + 3' 29'.      |

$$[\alpha]_D = + 156' \cdot 9.$$

2. 10 c.c. of the above neutral solution were diluted with 10 c.c.

\* Gamgee and Jones, "On the Nucleoproteids of the Pancreas, Thymus, and Suprarenal Gland, with especial Reference to their Optical Activity," 'Roy. Soc. Proc.', vol. 71 (1903), p. 385.

† Kossel and Neumann, 'Ber. d. Deutsch. Chem. Ges.', vol. 27, p. 2215.

of distilled water and the resulting solution was examined polarimetrically.

$W = 1.109$  grammes;  $V = 200$  c.c.;  $L = 200$  m.m.;  $\alpha = 1^{\circ} 43'$ .

$$[\alpha]_D = +154^{\circ}2.$$

3. 10 c.c. of the solution used in the last experiment were further diluted with 10 c.c. of distilled water and the resulting solution was examined.

$W = 1.109$  grammes;  $V = 400$  c.c.;  $L = 200$  mm.;  $\alpha = +0^{\circ} 52'$ .

$$[\alpha]_D = +156^{\circ}4'.$$

The above observations indicate that solutions of the nucleic acid of the thymus are powerfully dextro-rotatory, but that the specific rotation of neutral solutions does not vary appreciably with dilution, the variations in the results of the three sets of observations recorded above falling within the probable limits of error. Similar results had already been obtained with solutions of the nucleoproteid of the pancreas, although the limits of dilution in that case were not so great as in the present instance.

*On the Influence of the Reaction of the Solution on the Optical Activity of the Nucleic Acid of the Thymus Gland.*

The observations about to be referred to indicate a very remarkable influence exerted by the reaction of the solution on the optical activity of the nucleic acid under discussion. The rotation is notably influenced by the acidity of the solution; it reaches a maximum at a certain degree of acidity and then decreases. On the other hand, the addition of ammonia in sufficient proportion will render a solution of thymus-nucleic acid optically inactive, though neutralisation of the acid will restore its pristine activity. It is to be noted, however, that there is no abrupt change around the neutral point, a statement which is illustrated by the fact that two solutions of equal concentration may be prepared which are undistinguishable in so far as their optical rotation is concerned, one of which is faintly, though distinctly, acid to litmus, while the other is alkaline.

4. 25 c.c. of the original neutral solution of nucleic acid employed in the first set of experiments were made decidedly acid by the addition of a trace of 20 per cent. acetic acid. The change of volume was so small as to be negligible. The solution was then subjected to polarimetric examination with the following results:—

$W = 1.109$  grammes;  $V = 100$  c.c.;  $L = 200$  mm.;  $\alpha = +3^{\circ} 30'$ .

$$[\alpha]_D = +157^{\circ}8.$$

5. 25 c.c. of the original solution were correspondingly made distinctly alkaline with ammonia and polarimetrically examined :—

$$W = 1.109 \text{ grammes ; } V = 100 \text{ c.c. ; } L = 200 \text{ mm. ; } \alpha = +3^{\circ} 31'.$$

$$[\alpha]_D = +158^{\circ} 7.$$

The two above sets of experiments show that determinations of the optical activity of thymus-nucleic acid may be made in a neutral or quasi-neutral fluid, without fear of variation caused by inaccuracy in observing the point of exact neutrality. The following experiments, however, demonstrate that the rotation is markedly changed by the addition to a neutral solution of thymo-nucleic acid either of a considerable amount of acetic acid or of ammonia.

6. 20 c.c. of the original solution were treated with one-tenth of a c.c. of 20 per cent. acetic acid and the solution was polarimetrically examined :

$$W = 1.109 \text{ grammes ; } V = 100.5 \text{ c.c. ; } L = 200 \text{ mm. ; } \alpha = +3^{\circ} 33'.$$

$$[\alpha]_D = +160^{\circ} 4.$$

7. 10 c.c. of the solution used in 6 were treated with 0.3 c.c. of 20 per cent. acetic acid and polarimetrically examined :

$$W = 1.109 \text{ grammes ; } V = 101.5 \text{ c.c. ; } L = 200 \text{ mm. ; } \alpha = +3^{\circ} 36'.$$

$$[\alpha_D] = +164^{\circ} 7.$$

Up to this point we observe an increase in the specific rotation of the nucleic acid. If, however, as in the two following experiments, the amount of acetic acid is increased, the optical rotation undergoes diminution.

8. 10 c.c. of the original solution were treated with 1 c.c. of 20 per cent. acetic acid and then polarimetrically examined :

$$W = 1.109 \text{ grammes ; } V = 110 \text{ c.c. ; } L = 200 \text{ mm. ; } \alpha = +2^{\circ} 29'.$$

$$[\alpha]_D = +123^{\circ}.$$

The remarkable influence of solution of ammonia is illustrated by the following observations :—

9. 20 c.c. of the solution which had been used in observation 8 were treated with 0.5 c.c. of 10 per cent. solution of ammonia and polarimetrically examined :

$$W = 1.109 \text{ grammes ; } V = 102.5 \text{ c.c. ; } L = 200 \text{ mm. ; } \alpha = +2^{\circ} 40'.$$

$$[\alpha]_D = +123^{\circ} 4.$$

10. The solution used in experiment 9 was treated with an equal volume of 10 per cent. ammonia and the resulting solution examined :

$$W = 1.109 \text{ grammes ; } V = 205 \text{ c.c. ; } L = 200 \text{ mm. ; } \alpha = +0^{\circ} 35'.$$

$$[\alpha]_D = +50^{\circ} 8.$$

11. The solution used in experiment 10 was further diluted with an equal volume of 10 per cent. ammonia, when the solution was found to be optically inactive.

Our observations have shown us, as has been mentioned at an earlier part of this paper, that the diminution or abolition of optical activity which is induced by alkalies in solutions of thymo-nucleic acid are not permanent, the addition of acid restoring the primitive optical condition.

Bülow has shown\* that the optical rotation of proteids varies with changes in the reaction of their solutions, and Framm† studied especially the alteration brought about in the specific rotation of gelatine by the addition of acids or alkalies. The alterations observed by Framm, however, were probably due to fundamental chemical changes brought about by the acid or alkali on the proteid. This reasoning cannot, however, be applied to the case of the nucleic acid of the thymus gland, seeing that the addition of acid to an alkaline solution restores the optical activity.

At the suggestion of one of us (A. G.), Dr. Thomas B. Osborne‡ has determined the optical activity of the nucleic acid which he separated from the wheat embryo, and to which he applied the name of tritico-nucleic acid. Dr. Osborne§ has found that this nucleic acid is dextrorotatory, though the degree of rotation is considerably influenced by the concentration of the solution. A solution containing 4 per cent. of tritico-nucleic acid possessed a specific rotation  $[\alpha]_D = +73^\circ$ .

\* Bülow, "Ueber aschefreies Eiweiss," 'Pflüger's Archiv,' vol. 58 (1894), p. 207.

† Framm, "Untersuchungen über die specifische Drehung des  $\beta$ -Glutin," *ibid.*, vol. 63 (1897), p. 144.

‡ T. B. Osborne and I. F. Harris, "Die Nucleinsäure des Weizenembryos," 'Zeitschr. f. Physiol. Chemie,' vol. 36, heft 2 (September, 1902), p. 85.

§ T. B. Osborne, "The Specific Rotation of the Nucleic Acid of the Wheat Embryo," 'Amer. Journ. of Physiol.,' vol. 9, No. 2 (issued April 1, 1903), p. 69.

"New Investigations into the Reduction Phenomena of Animals and Plants.—Preliminary Communication." By J. B. FARNER, F.R.S., and J. E. S. MOORE, A.R.C.S. Received May 29,—Read June 18, 1903.

The attention given by numerous investigators to those periodically recurring nuclear changes known as reduction divisions, has so far apparently resulted only in an increasingly wide divergence of opinion, both respecting the nature of the process and its significance, but there are nevertheless a number of cardinal facts upon which all are fairly agreed. It is generally admitted, for example, that during the reduction processes the number of the chromosomes is halved; that this is everywhere effected during the period of rest immediately proceeding the mitoses in question; that two consecutive mitoses appear to be intimately connected with this process, but the first of these, the heterotype division, is generally markedly distinct from other nuclear divisions; consequently it would seem probable that the explanation of the reduction in the number of the chromosomes, of reduction generally, is to be obtained through a minute study of the heterotype or synaptic prophase in a large number of animals and plants. With this conception before us, we have sought out in each case as complete and unbroken a series as possible, illustrating the stages by which the synaptic spireme thread is converted into the reduced heterotype chromosomes; and the results of our investigations have not only been such as to considerably modify the conception of the process as already set forth by ourselves in a number of former memoirs, but at the same time to indicate a possible reconciliation between most of the different views which have been and are held by other investigators.

The two main theories as to the nature of reduction may be shortly stated. In the first we have the process regarded as a qualitative and quantitative division of the chromatin by the ultimate separation into daughter nuclei of entire somatic chromosomes. It is assumed that such entire chromosomes may be temporarily united during the early prophase of the heterotype division, and thus a "pseudo-reduction" (Häcker) be brought about. But during the homotype division these chromosomes are separated and pass in their entirety to one or other of the daughter nuclei. It is held by most investigators that the final separation is effected during the second or homotype division, the heterotype being characterised by the separation of the longitudinally split halves of the chromatic thread-work.

The second view is that which was strongly urged by Brauer, and is now held by a large number of both zoological and botanical investigators. According to this conception the identity of the original somatic

chromosomes becomes lost at the close of the cycle preceding the synaptic rest; and they are replaced by half the somatic numbers of new ones which first become visible in the prophase of the heterotype division. During their formation these reduced chromosomes become longitudinally divided twice, in planes at right angles to each other, and in this way the frequently observed rapid succession of hetero- and homotype divisions is accounted for, the fission for both mitoses having taken place almost simultaneously. Many instances have been described of the synaptic chromosomes presenting the appearance of doubly split threads, and this second view of the reduction process consequently appears to rest upon quite as sound a basis of observation as the first. As they stand, the results of existing investigations upon these matters would appear to lead to a belief that the reduction processes are diverse in character and cannot possess the theoretical importance which it has been suggested may attach to them.

A re-investigation of the whole matter has, however, convinced us that neither of the above interpretations is correct. We find that the appearances, hitherto supposed by nearly all observers\* to indicate the mode of formation of the heterotype chromosomes, do not seem to have been correctly apprehended, this being due to certain important stages in the process having escaped adequate appreciation. The entire metamorphosis is admittedly excessively difficult to observe, but the whole may be traced in a manner which seems to leave no room for doubt that both the appearance of a double longitudinal fission, and the origin of the heterotype daughter-chromosomes from split threads, are quite illusory. Moreover, in the numerous plants and animals in which we have followed out the process, we have obtained remarkably concordant results, and we think that the explanation we are now able to give of the origin of the reduced chromosomes is one which incidentally accounts for the many peculiar figures and vagaries that have so frequently been observed and remarked upon.

At the end of the synaptic rest, that is, in the prophase of the heterotype division, the spireme thread certainly undergoes a longitudinal fission (Figs. 1 and 2), often before it segments into the reduced number of chromosomes (*Osmunda*, *Lily*, *Aneura*, among plants; *Salamander*, *Axolotl*, *Blatta*, among animals). Following, however, upon this fission, which may result in a wide divarication of the longitudinal halves of the split thread work, comes a stage when the

\* Schaffner, in 1897 ('*Bot. Gazette*') suggested that in *Lilium Philadelphicum* the process of reduction is essentially identical with that described in this paper. The value of his correct observations was obscured by errors in other respects, and they have lain practically unnoticed, perhaps on this account.

Korschelt ('*Zeit. Wiss. Zool.*' vol. 60, 1895) describes a peculiar process for *Ophryotrocha* that is easily brought into line with our observations, though hitherto it has been regarded as an isolated and peculiar case.

spireme contracts, and, as this phase progresses, the threads are pulled into more and more parallel positions (Figs. 2 and 3); and, if polarisation is strongly marked, as in most animals, the threads are seen to take the form of loops, or large U-shaped figures. Although still showing longitudinal fission, the sides of these loops approximate once more, and eventually nearly all signs of the original split are obliterated. But, even at a later stage, careful search often reveals the original opening running along the sides of the loops. This method of formation of the U-shaped chromatin bands, and the final approximation of their limbs, has given rise to a complete misunderstanding of the ensuing phases; the approximated limbs of the loop having been regarded as the longitudinally split halves of the spireme thread, and the great increase in their thickness having been supposed to be due to a large contraction in the length of the spireme.

The full sequence in the production of the loops can only be made out in very carefully prepared material, and as a result of a comparison of sections with uncut cells. The chromatin, indeed, during these stages seems to be in a condition very sensitive to unfavourable manipulation, and we have reason to think that the quite unnecessary length of embedding processes so frequently resorted to may be greatly responsible for the failure to recognise the true sequence of events. Every cytologist who has examined thick sections, or uninjured cells, in which the early heterotype chromosomes are shown, must have been struck with the appearance of forms composed of rods, often twisted on themselves with their limbs open at one end, and forming at the other a conspicuous loop, such loops being in reality nothing more than the bent middle portions of the original U-shaped spireme segments (Fig. 4). The bent portions of the loops, however, mark the place at which, during the metaphase, the heterotype loop will break apart into the two chromosomes, of which it is composed. It sometimes happens that, even at this stage, traces of the longitudinal fission can be distinctly seen, and it is the persistence or reappearance of this fission which has been taken for a second longitudinal split. The number of the chromatic loops corresponds to the reduced number of the chromosomes, and thus there is direct evidence that each loop is really bivalent in the sense in which the term was used by Häcker, but our view of the actual process of the formation of the loops, and of the subsequent course of events, does not coincide with the conclusions reached by this investigator.

When the bivalent chromosomes, loops or rings, become arranged on the spindle (Fig. 5), they split asunder in such a way that one limb of the loop passes into each daughter nucleus, and consequently it will be apparent that their division cannot be regarded as the completion of any longitudinal fission, but as a transverse separation of the chromosomes originally united together end to end in the bivalent loop ring or rod

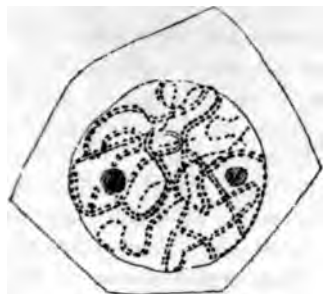


Fig. 1.

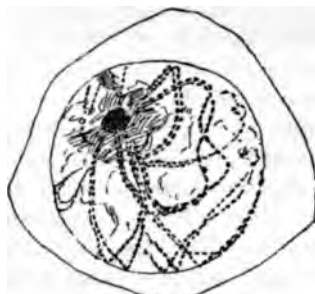


Fig. 2.

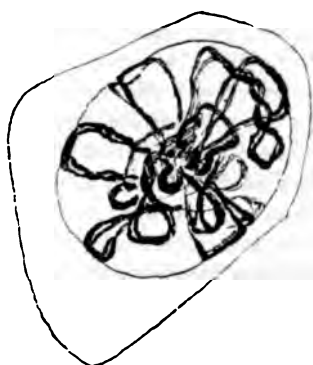


Fig. 3.



Fig. 4.

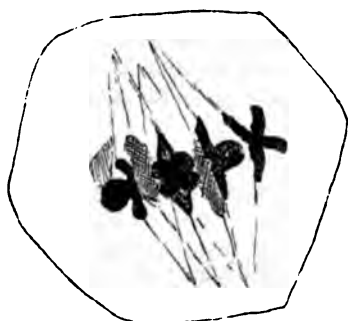


Fig. 5.



Fig. 6.

In *Blatta*,\* the original longitudinal split is, as we have said, apparent

\* The investigation of spermatogenesis in this insect was undertaken by Mr. L. Robinson, in conjunction with ourselves. His results will be presented in the final memoir.



while the rings are opening out on the spindle and before the united chromosomes of which it is composed have separated, and although in some cases it is more or less concealed, this early fission rapidly reappears, and the remarkable figures seen in the anaphases of *Tradescantia* or Salamander, thus find their explanation.

The deceptive appearances presented by lilies at this period also find an intelligible explanation when the mode in which they are attached to the spindle fibres is borne in mind, and a remarkable confirmation of this is forthcoming in the fact, which seems to have hitherto escaped observation, that in some cases the daughter-chromosomes, like those of *Tradescantia*, clearly show their original longitudinal split (Fig. 6). This original longitudinal fission of the spireme thread which is usually visible in the retreating daughter elements is retained in some, probably in all, cases as a preparation for a succeeding homotype division.

It would thus appear from the preceding observations, that the synaptic rest, culminating in the heterotype mitosis, is a phase specially intercalated in the reproductive cycle. In it a reduction of the number of the chromosomes is brought about by their adhesion in pairs, but with the inception of karyokinetic activity the spireme thread undergoes the longitudinal fission characteristic of ordinary somatic division, although the actual separation of these longitudinal halves is deferred until the next mitosis. Thus the heterotype division not only seems to be different in kind from an ordinary mitosis, but in this very fact probably lies the reason of the extraordinary diversity of form so often obvious among the chromosomes in this, as compared with any other, type of nuclear division.

We have purposely refrained in this communication from criticising the results of others, and from discussing the general bearings of our own interpretation of the phenomena upon heredity and other matters. We have done so because we think this part of the subject will find a more appropriate place in a memoir now in preparation, wherein the evidence for our conclusions will be fully set forth.

The illustrations that accompany this paper are intended merely to serve as diagrams explanatory of the more important stages of the heterotype division.

#### EXPLANATION OF THE FIGURES.

1. Spireme thread showing longitudinal fission.
  2. Looping together of the split spireme.
  3. Same at a later stage.
  4. The loops have separated, and the longitudinal fission cannot always be recognised.
  - 5 and 6. Stages in the separation of the daughter-chromosomes at the equatorial plate.
-

“ Evolution of the Colour-Pattern and Orthogenetic Variation in certain Mexican Species of Lizards, with Adaptation to their Surroundings.” By HANS GADOW, F.R.S. Received May 22, —Read May 28, 1903.

[PLATES 3—5.]

I.—*Introduction.*

The late Th. Eimer\* has shown that the variations of the colour-pattern of the European *Lacerta muralis* proceed each on definite lines until a certain stage is attained which is characteristic of the race, or variety, in question. This mode of development he has termed *orthogenetic*. As a rule, the successive changes in the colour-pattern of lizards, are as follows: First longitudinal stripes, then dissolution of the stripes into spots, then confluence of the spots in a transverse direction so that a cross-barred pattern is produced, lastly a uni-coloured appearance. There are some lizards which pass through the whole scale during their growth from youth to old age. Others again stop short at perhaps the second, or even at the first stage. This phenomenon of arrested development he has termed *epistasis*; *genepistasis* when applicable to a whole association of individuals, be such a community a local race, representative of a sub-species, or of the dignity of specific or even higher rank; *ontepistasis* when the same phenomenon applies only to individuals, for instance, if a specimen of a normally cross-barred kind should stop short at the spotted stage. Again, there are precocious individuals, races and species, which, instead of passing through the whole scale, begin already with the second, or another later stage. Moreover, there are new and further departures which, leading beyond the normal condition, are liable ultimately to accumulate, or to consolidate into the formation of new races, &c. All these changes are, as a rule, initiated, at least they are earlier and more frequently visible in the males, while the females often remain at a lower, more juvenile, level. Lastly, these changes begin near the tail and proceed wave-like forwards, so that, for instance, the shoulder region may be still in one stage, while the lumbar region has already assumed the final aspect. This is Eimer's law of postero-anterior development, and since these successive changes, like successive waves, pass not only over the bodies of individuals of one kind, but also over species and genera (provided they be arranged as striped, spotted, barred and uni-coloured forms), Eimer suggested the term *undulatory development*.

\* “ Untersuchungen ueber das Variiren der Mauereidechse, ein Beitrag zur Theorie von der Entwicklung aus constitutionellen Ursachen, sowie zum Darwinismus,” ‘Arch. f. Naturg.,’ vol. 47 (1881), pp. 239—517, plates 13—15.

The general applicability of Eimer's "laws" has been tested with favourable results in all classes of vertebrata, although naturally in many cases the detailed investigation is obscured by cœnogenetic omissions and other modifications.

Cope\* has repeated Eimer's observations by the study of several kinds of the American lizard-genus *Cnemidophorus*, and he has illustrated several successive changes from stripes to cross-bars in *C. tessellatus* and *C. gularis*. But he has split the whole genus into a bewildering number of species and sub-species, not allowing sufficient scope for individual variation, and he has apparently not exemplified his points on specimens from the same locality. An attempt to study these and similar changes minutely and in series, and to connect them with the prevailing conditions of the surroundings, has hitherto not been made.

I have been fortunate during the last summer in collecting material sufficient to show, first, the amplitude of individual variation; secondly, that there exist in the various kinds of *Cnemidophorus* several modes of attaining the same end, that each of these modes may occur, and proceed to a moderate extent individually, carrying the individual out of its normal way, and lastly, that some of these changes seem to be governed by the physical conditions (constitutional or organic, and the prevailing features of the terrain), while sexual selection plays none, and natural selection but a secondary part.

Such inquiries cannot be made unless the exact conditions of the terrain, and the habits of the creatures are observed. My collections and observations were made in steaming hot tropical forests, in hot and dry lowlands, and on the more temperate table-lands of Southern Mexico. My material has been compared with that in the National Collection, and I have to thank Mr. Boulenger for his ever-ready invaluable help and advice.

## II.—*The Structural Variations and the Mutual Affinities of Various Kinds of Cnemidophorus.*

It is a tedious, but necessary, preliminary to record the amplitude of the so-called structural variations within the recognisable kinds of *Cnemidophorus*. Whether these be called species, sub-species, or races is a matter of personal inclination, but the smaller the structural differences, the more significant will be the differences in pattern and coloration in such closely allied forms, provided these live under other physical conditions. All the various *Cnemidophorus* and *Ameiva* live on the ground, never climbing trees hunting for insects.

I recognise five definable forms of *Cnemidophorus* as occurring in Southern

\* 'Amer. Phil. Soc. Proc.,' 1885, p. 283; and 'Report of the U.S. National Museum,' 1898, p. 569.

Mexico; *C. deppei*, Wiegman; *C. guttatus*, Wiegman; *C. striatus*; *C. mexicanus*, Peters; *C. bocourti*, Boulenger.

The number of the small granular scales on the back varies extremely. Counted in transverse rows across the body, such a row contains in *C. deppei* from 93 to 150 and more, regardless of sex and age; in *C. guttatus* from about 100 to 180. The relative size of these scales is consequently not a trustworthy character. The number of supra-ocular plates is normally 4 in *C. mexicanus* and *C. bocourti*, but sometimes the most posterior plate is very small, separated from the rest, or absent. In *C. guttatus* and *C. deppei* the number is normally reduced to 3.

The posterior edge of the collar on the neck is abrupt, being formed by the enlarged scales themselves, in *C. bocourti*, while in *C. guttatus* and *C. striatus* the edge is formed by one or more complete series of granules. In the majority of adult *C. deppei* there is one complete series of granules; several females show one granule between each scale, and in others the collar ends abruptly without granules. Lastly in *C. mexicanus* this character breaks down completely, independent of age and sex.

Number of enlarged scales on the forearm: 2 rows in *C. deppei* and *C. guttatus*; 3, rarely 2 in *C. bocourti*, 3 in *C. mexicanus*.

Slightly enlarged granules or scales on the posterior aspect of the forearm: the whole posterior surface is uniformly granular in *C. guttatus*; a few slightly enlarged scales near the elbow in some *C. deppei*; a cluster nearer the hand, almost imperceptible in *C. striatus*; several slightly enlarged rows in some *C. deppei*; several long rows of distinctly enlarged scales in *C. mexicanus* and *C. bocourti*.

A separate cluster of slightly enlarged granules or scales occurs on the hinder surface of the upper arm (so-called *postbrachials*) near the elbow, separated from the large scales by small granules; *C. guttatus*; some *C. striatus* and some *C. deppei*. No such cluster occurs in *C. mexicanus*, *bocourti*, most *deppei* and some *striatus*.

The enlarged scales which protect the thighs' anterior and inner surface are arranged in several rows; 6—7 in *C. deppei* (7), 8 or 9 in *C. bocourti* 8 or 9 in *C. mexicanus*, rarely 8, mostly 9 to 12 in *guttatus* and *striatus*.

Number of rows of enlarged tibial scales: 2 in most *C. deppei* increasing towards 3, remaining at 2½ in other *deppei*, in *striatus* and *bocourti*; increased to 3 complete rows in some *deppei*, in *guttatus*, some *bocourti* and in *mexicanus*.

The cluster of enlarged preanal scales is separated from the regular ventrals by about half-a-dozen short, transverse rows of small roundish scales, so that there is a distinct break between anals and ventrals: *C. guttatus* and *striatus*. The preanal cluster is separated from the ventrals by but few scales, which are arranged rather irregularly, and are in size not so abruptly smaller than the ventrals, and they form a narrow isthmus: *C. deppei*, *mexicanus*, *bocourti*.

The variations in the number of femoral pores can be expressed

diagrammatically. It should, moreover, be observed, that the number of pores on the right and left thighs not unfrequently differ by one or two.

|                       |       |               |                |             |       |       |                            |       |       |       |       |
|-----------------------|-------|---------------|----------------|-------------|-------|-------|----------------------------|-------|-------|-------|-------|
| Number of pores . . . | 15    | 16            | 17             | 18          | 19    | 20    | 21                         | 22    | 23    | 24    | 25    |
|                       | ..... | bocourti..... | .....          | .....       | ..... | ..... | .....                      | ..... | ..... | ..... | ..... |
|                       |       | .....         | mexicanus..... | .....       | ..... | ..... | .....                      | ..... | ..... | ..... | ..... |
|                       |       |               | .....          | deppei..... | ..... | ..... | .....                      | ..... | ..... | ..... | ..... |
|                       |       |               |                | .....       | ..... | ..... | guttatus and striatus..... | ..... | ..... | ..... | ..... |

None of these characters, usually applied in "keys," are absolutely reliable when considered singly and when used to establish categories, but taken together they are sufficient to define the five kinds of *Cnemidophorus* which occur in Southern Mexico. In addition, there is the size of the adult, the colour-pattern and above all the mode of its change. This brings us to a point of general importance. Two given forms may structurally approach each other so closely, and the differences still existing may be of such slight weight, that we can separate them only by their pattern of colour, and if this happens likewise to be in a changing mood, the two sets of creatures can no longer (or not yet) be regarded as different, nor as geographical races when they live in the same place. Where the physical conditions are exactly the same, monotonous, there occurs only one species of the same genus, for instance, in a desert, on a treeless prairie, in a dense forest; but if the terrain is varied, although for all practical purposes remaining the same, there is as likely as not more than one species. If these are closely allied we have a chance of correctly connecting their differences with their surroundings. This applies to *C. mexicanus* and *C. bocourti*. Again, close allies afford the same chance if they inhabit markedly different localities, no matter whether these kinds of terrain are geographically distant or close together. An instance of this are *C. guttatus* and *C. striatus*. Now, *C. bocourti* and *C. guttatus* are in most structural characters extremes of each other, but both are the spotted representatives of their nearest allies in terrain which produces an abundance of broken shade. Moreover, *C. mexicanus* and *C. bocourti* stand as larger sized modifications in the same relation to *C. scelineatus* of the Southern United States as *C. guttatus* and *C. striatus* do to the small and strongly striated *C. deppei*, which is the southern counterpart of *C. scelineatus*. It is also significant that it is not *C. guttatus* but *C. striatus* with which *C. deppei* has more structural affinity, and that both these forms occur partly together, at least in the Tehuantepec district.

III.—*Evolution and Variation of the Colour-Pattern.**Cnemidophorus deppei*, Wieg. (fig. 1, Pl. 3).

The pattern of this small species is always striped, the white lines\* 1 to 4 contrasting sharply with the alternating dark fields, but there is great variation within the midregion enclosed by stripes 4—4.

*Stage A. 8 White Stripes.*—Specimens with only 4 pairs of white stripes and with a narrow uniformly dark centre field are rare.

*Stage B. 9 White Stripes.*—Represented by about 24 per cent., babies and adult of both sexes. The white central stripe is either still short and very thin, or it reaches from the neck to the tail. Occasionally it is represented only by a faint row of white dots and streaks, and the two lines 4—4 combine in front and behind.

*Stage C. 10 White Stripes.*—Represented by about 40 per cent., comprising babies and adult. The original midfield between stripes 4—4 is divided by a black centre line which exhibits every stage from separate specks or long dots to a complete streak which extends over the greater length of the trunk, leaving, however, the new pair of white lines 5—5 confluent in front and behind. The modification from Stage B to C seems to be brought about by a broadening of the originally impaired centre line 5, in the middle of which appear tiny black specks which increase longitudinally, while the white line broadens out. In Stage C these new white lines are further emphasised by black pigment which is more densely deposited between them and the lines 4—4.

*Stage D. 11 White Stripes.*—Represented by about 30 per cent., all adult. This condition is a further development of Stage C. The original midfield between 4—4 has become still broader. The same applies to the black centre line, which, beginning on the middle of the trunk, is rent asunder, owing to the appearance of new white tissue. This splitting of the black line is continued, until at last a new white and long stripe 6 is produced, which, in old specimens, may extend over nearly the whole length of the back.

The Stages A to D are so gradually connected with each other that it is impossible to refer every specimen to one or other of the four categories. This applies especially to those which show only 8 white stripes, but with the centre field between 4—4 broad and rather pale, brown or grey, much paler than the other dark fields, although distinctly darker than the lines 4—4. The centre of this midfield is

\* The white lines are counted proceeding from the sides of the body towards the middle of the back. The first line passes through the outer ear, over the root of the upper arm, along the sides of the body and then on to the thigh. The second line extends from the upper margin of the eye to the hip joint. The third begins at the posterior occipital corner.

sometimes lightened up, indicating transition to Stage B; or blackish pigment is collected in the centre and also on the inner borders of lines 4—4, so that Stage C seems to be foreshadowed. On the other hand, there are a few aged specimens which suggest, by the mottled and irregular distribution of the pigment within the broad centre field 4—4, that they have relapsed from an 11-striped to the 8-striped condition.

*Another Field of Variation* in pattern and colour are the sides of the body, from the ear-stripe, No. 1, down to the ventral scales. This lateral region is very liable to become "ornamented" with white roundish spots or patches, arranged in one or two, rarely in three longitudinal rows, which begin at the thighs and decrease in distinctness towards the arms. There are several degrees:—

1. The stripe No. 1 is complete and there is no lateral row. Observed in females only.

2. The stripe 1 is complete and below it is a short, or faint, line, continuous or as interrupted spots; rather frequent in female or very young 9-striped specimens.

3. Stripe 1 is more or less broken up into a string of white heads; below it follows a row of large, roundish white spots: one 8- and one 9-striped female, and one 10-striped male; or there are two very conspicuous rows of spots: the majority of males, nearly all with 10 or 11 stripes.

4. Same as 3, but not only line 1, but also line 2 is broken up into white beads, and the two lateral rows are very conspicuous. Observed in large and small males.

The development of lateral spots is, with individual exceptions, pre-eminently a feature of vigorous males. The same applies with still greater force to the colour of the under parts. They are yellowish-white, or with a faint bluish tinge, in the young and in the females, but blue or almost black in males from the breeding season towards the "winter." The dark blue is most intense on the abdomen, on the chest, and on the narrow collar, extending over the under surface of the thighs and arms and suffusing the throat.

#### *Cnemidophorus guttatus*, Wiegman.

This species is restricted to the hot parts of tropical Mexico, and appears as two races, which structurally not distinguishable, are very different in their colour pattern. The striped race has hitherto been found only on and near the Isthmus of Tehuantepec, where it inhabits the same kind of terrain as the small *C. deppei* but with less scanty vegetation. The spotted race is restricted to the open forests with dense undergrowth, ranging from near Vera Cruz to the eastern slope of the Isthmus.

**C. GUTTATUS VAR. STRIATA** (fig. 2).—The young of the first year are decidedly dark above; only the first pair of stripes is white, although thin and sometimes vanishing towards the arms; the other stripes are so little pronounced that they appear only under certain lights as greenish bronzy bands, somewhat lighter than the ground colour.

Older specimens exhibit variation from 6 to 7 or 8 white stripes, even with an incipient 9th, and these variations can be grouped as follows:—

**Stage A. 6 Stripes.**—In a specimen 80 mm. in length the third pair of stripes is united on the neck. The enclosed midfield is dark and shows very faint, pale mottlings, due to an irregular double row of spots on the lumbar region and lower back, confluent on the middle of the back.

**Stage B.**—The 3rd pair of stripes forms parallel lines. On the mid-field conspicuous white spots form a double row on the middle of the trunk, single, by confluence towards the shoulders. Further modification of this double central row (equivalent to stripes 4) leads either to Stage C or to D.

**Stage C. 7 White Stripes.**—The central stripe, formed by fusion of the double row, is composed of white beads, or beads and a continuous stripe of variable extent.

**Stage D. 8 White Stripes.**—The double row is joined into one on the neck, but is continued over the back in two conspicuous lines, 4-4, which on the lumbar region are each dissolved into a row of spots.

**Stage E. 9 White Stripes.**—The same as D, but in the mid-line of the back, or on the lumbar region, has appeared a short row of white spots, indicating a 5th unpaired line.

In older specimens the first pair of lines becomes faint and shortens from before backwards, and lateral spots, below this line, appear in two rows. Additional small spots make their appearance near the tail and on the lumbar region in the dark fields between the lines 1-2 and 2-3.

The colour of the under parts varies but little: yellowish-white in the females, suffused with pale blue in the males, and the latter have always a narrow blackish collar.

**C. GUTTATUS VAR. GUTTATA** (fig. 3, Pl. 4).—The important features of this very dark race are the complete breaking up of the 4th and 3rd pair of lines into whitish-yellow spots, the breaking up and fading of the 2nd and 1st pair of lines, and, lastly, the complete disappearance of the spots from the root of the tail forwards over the lower back.

These changes are gradual and proceed regularly with age.

In very young specimens all the underparts are uniformly white, including the collar. Lines 1 and 2 above are still pronounced white stripes, although sometimes partly broken into short streaks, and fading towards the arms. The original stripes 3 and 4 are already



dissolved into rows of about 25 small, pale dots, reaching from the neck to the tail. With advancing age these dotted rows become faint, whilst further forwards they become more pronounced. Then they enlarge slightly, approaching thereby, and ultimately neighbouring spots of the rows 3 and 4 fuse with each other, so that the back assumes a slightly yellow-barred appearance.

Especially the old males, with vanishing stripes 1 and 2, and without specks on the lower back, do not suggest in the slightest way that these creatures started originally with 4 pale stripes.

The underparts are more or less dark blue in old males, yellowish or greenish-white, suffused with blue, in the females. The collar is invariably blackish.

*Cnemidophorus mericanus*, Peters (fig. 4, Pl. 4).

This rather large lizard is an inhabitant of the southern table-land, provided its elevation remains well within the temperate zone. The terrain is rather barren; always devoid of luxurious or dense vegetation. During their growth these lizards pass through an extraordinary series of changes in their colour pattern.

*Stage A. With 6 white stripes.*—The young, up to 60 mm., possess three pairs of complete white stripes, sharply alternating with narrow, dark brown fields.

*Stage B.*—Pale, faint spots appear in the fields between the stripes 1—2 and 2—3, and the midfield between 3—3 becomes lighter in this way, that the dark pigment is arranged in tiny dots, or in more continuous lines against the inner borders of the 3rd stripes; and occasionally there appears also a darker central streak. Then, with a head to tail length of about 70 mm., the spots in the fields become lighter, more numerous, and arrange themselves in double rows, and the midfield 3—3 becomes broader and greenish.

*Stage C.*—When the lizards approach the length of 100 mm. the double rows of field spots become transversely confluent, and the lateral stripes 1 and 2, hitherto very conspicuous, become dull, and lose their sharp contours. Owing to the confluence of the pale spots each field is now broken up into some 20 to 22 dark cross-bars. These bars become darker, sometimes black brown, and encroach upon the dissolving white stripes 1, 2, and 3, whilst the remaining parts of these lines join, or merge into the adjoining confluent transverse spots, which are still expanding.

*Stage D.*—Ultimately the whole back and the sides of the body assume a very complex pattern; brown, pale brown, and white colours, mottled or vermiculating, in the main, however, decidedly cross-barred. In some cases the black bars from the right and left meet across the back. The extent to which the longitudinal pale lines

disappear, or remain more or less vestigial, varies extremely, and in the adult of both sexes, strictly speaking, the detail of the whole complicated pattern is scarcely the same in two individuals from the same locality.

The midfield, between stripes 3—3, although unimportant, since it never produces any marked characters, undergoes individual changes which remind us of those which occur in other species. As a rule the midfield becomes lighter in the way described above, and it turns green in immature specimens; later it becomes pale grey-brown, and ultimately more or less mottled and barred with dark pigment. But in one baby of 59 mm. there is a faint, unpaired, central streak, which extends back from the occiput; and in a specimen of 87 mm. this line is still paler, almost white, bifurcating and extending right down to the rump. These lines represent undoubtedly the 4th pair of stripes, otherwise absent in *C. mexicanus*. Sometimes, however, pale spots appear in this midfield, arranged in two rows, as indications of the 4th pair of lines. On the other hand, there is in a few cases a distinct narrow, dark line in the centre of the green field.

The under parts of these lizards are yellowish-white, with a reddish tinge on the under surface of the hind limbs, and on the throat, while the under surface of the tail and the whole of its terminal half are often orange to almost brick-red. The collar is never dark. The chest and abdomen of old specimens, especially males, are suffused with greenish or faint blue, while the basal edges of the scales are blackish. After removal of the horny portion of the epidermis the under parts appear quite blue-black, owing to thick pigmentation in the malpighian and in the cutaneous strata.

*Cnemidophorus bocourti*, Blgr. (fig. 5, Pl. 5).

Structurally, this lizard is but a slight variety of *C. mexicanus*, with which it shares the same distribution, except that it is more partial to denser vegetation. It is spotted instead of cross-barred or striped, standing in this respect in the same relation to *C. mexicanus* as *C. striatus* does to *C. guttatus*.

All the three stripes are broken up into numerous yellow spots, and a row of equally numerous spots is developed in the fields, and below the original line 1, so that there are in all about 12 to 14 rows of spots across the body. On the lumbar region the spots are more irregular and crowded; towards the shoulders they become scarcer, and further forwards they disappear altogether, while faint traces of the original pale lines 1 and 2 remain visible.

In very old specimens the spots are small and irregular, and restricted to the lumbar region, the rest of the back being spotless brown, with a warm reddish tint.

The under parts of neck, throat, and arms are greenish-white, yellowish on the tail; chest and abdomen are dark blue, mottled with white. Sometimes, not only in old males, faint blackish mottlings extend upon the collar, and even upon the throat.

Such spotted *C. bocourti* have hitherto been found in only a few, rather isolated districts. I myself found them in the immediate vicinity of the town of Oaxaca, amongst the tangled growth of shady trees and hedges. A large gravid female in the National Collection, from Santo Domingo de Guzman on the isthmus, and several immature specimens from the Sierra de Nayarit, Jalisco (oak forests) are intermediate in colour between *C. bocourti* and *C. mexicanus*. Others are known from "California."

*Ameiva undulata*, Wieg. (fig. 6, Pl. 5).

The only species of this otherwise South and Central American genus, which extends into Mexico, where it is an inhabitant of the hot and moist tropical open forest belt, frequenting open and sandy patches.

Very young specimens, about 45 mm. in length, are very dark brown, with two pairs of yellow lines extending from head to tail. In older specimens much black pigment is deposited on either side of stripe 1, which thereby is encroached upon and broken up into streaks and spots. The whole field between stripes 1 and 2 becomes mottled, or vermiculated with brown and black, the black disposing itself in irregular, incomplete cross-bars. Some females remain in this condition.

A further stage is entered upon by the appearance of one or more rows of patches in the field 1—2, at first pale brown, then gray, ultimately, white; small whitish spots and dots appear between stripe 1 and the central scales. This is typical of many adult females and immature males. In the final stage, characteristic of most adult males, the patches on the field 1—2 become confluent into a broad, irregularly bordered, very conspicuous white band, extending from the tail to the shoulder. The lateral spots are enlarged and combined transversely into pure white patches. Stripe 2 is completely overwhelmed by blackish pigment, only a narrow and faint streak remaining on the neck.

Some adult females remain at intermediate stages, the lateral spots and those of the original line 1 remaining small, while the newly-formed light row in the field 1—2 is represented by a pale gray band, bordered by black; the whole of stripe 2 remains as a faint, narrow, streak.

*Summary of the Evolution of the Pattern (fig. 7).*

Longitudinal white stripes can be dissolved into spots, and this breaking up proceeds from the tail forwards. On the other hand, pale spots can by confluence produce longitudinal stripes, e.g., in *Ameiva* and in the lines which appear in the centre field of *C. striatus* and *C. deppei*. Another mode of the production of white stripes is the concentration of the dark pigment along the borders of an existing dark band, while new, colourless tissue grows in the middle of such band, which ultimately is transformed into a white stripe flanked by a dark one. Or, in the case of the unpaired spinal band, this process may be reversed; dark pigment appearing in the centre of the broadening white band, which thereby is split into two white stripes. This process is repeated alternately, cf. in *C. deppei*, ranging from 8 to 11 stripes.

Confluence of pale spots in a transverse direction, accompanied by a massing of dark pigment along the newly-formed borders, leads to a pattern of cross-bars, cf. *C. mexicanus*. Uniform coloration is the last, highest, stage attainable.

Concerning *Cnemidophorus*, the various lines of evolution are the following; assuming as the starting point a small form like the typical *C. sexlineatus* with 6 strongly marked white stripes:—

1. In sandy terrain with sparse tufts of grass. Increased number of sharply marked stripes with tendency to increase from 8 to 11: *C. deppei*.

2. In the same terrain, but with less scanty vegetation. Usually 7 to 9 stripes which tend to break up into spots on the lower back, and reduction of the lateral stripe: *C. guttatus striatus*.

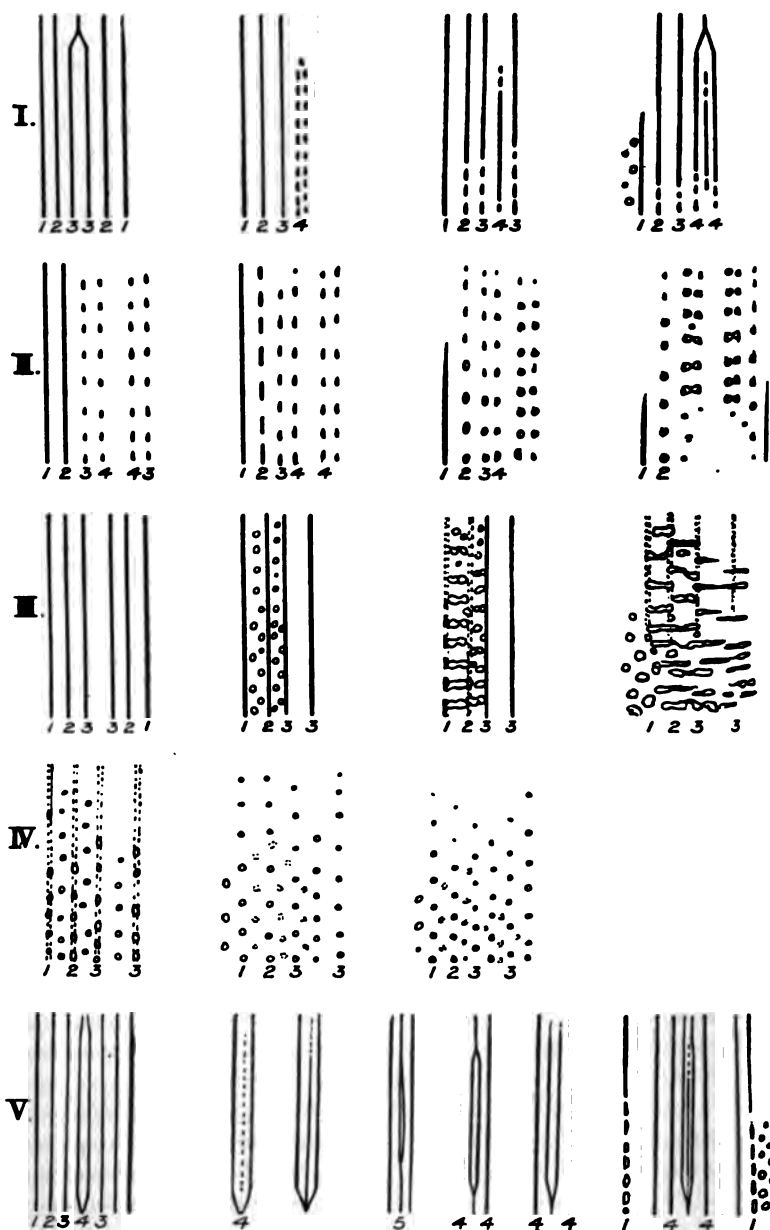
3. In open tropical forest, with much undergrowth. Fading of the lateral stripe; dissolution of the other stripes into numerous small spots, which disappear with age on the lower back: *C. guttatus guttatus*.

4. On the open table-land, with scattered spiny shrubs and hedges. Change of the young with 6 sharp stripes and pale spots on the dark bands to a cross-barred pattern: *C. mexicanus*.

5. Same localities as the last, but with more mixed vegetation. All the lines are broken up into spots, in addition to those on the intermediate parts: *C. bocourti*, a spotted race of *C. mexicanus*.

There can be no doubt about it that in the genus *Cnemidophorus* the permanently striped condition is the original, while the spotted is a secondary modification, upon which in turn follows the formation of cross-bars. Both the spotted and the barred forms have a tendency towards uniform coloration. This ultimate and highest stage is partly reached by *C. bocourti* and *C. guttatus*, without the interposition of a barred stage. Parallel cases are Cope's *C. semifasciatus* and *assclatus rubidus*, which are terminal side issues of the typically striped,

FIG. 7.



Diagrams showing the evolution of the colour pattern of *Cnemidophorus*. I. *C. guttatus striatus*. II. *C. guttatus guttatus*. III. *C. mexicanus*. IV. *C. bocourti*. V. *C. doppei*. The numerals 1, 2, 3, 4 indicate the identical homologous white lines or series of spots.

and then cross-barred *C. gularis* and *C. tessellatus* of Northern Mexico and of the Sonoran sub-region. But with no precise data for the natural conditions of these creatures, any further speculation would be unprofitable.

There is a continuous line of development leading from a completely striped form like *C. deppei* to another, *C. striatus*, in which the white stripes show an unmistakable tendency of breaking up into spots, until there are only spots left in *C. guttatus*, and this phenomenon means in this case the gradual preponderance of dusky pigment. On the other hand *C. deppei*, itself undoubtedly a descendant of a 6-striped form, has the tendency to increase the number of its stripes.

I connect these changes with the different features in the distribution of light which prevails in the various terrains on which these lizards live. Notice the peculiar distribution of sunlight and shade prevailing on the ground where strong light falls through dense vegetation; there are not many shadows, but plenty of shade, and this is interrupted by the familiar little sun images. Contrast this with the sharp alternation of bright light and shadows under a tuft of grass on sandy soil in glaring sunshine, where one blade reflects white light while the shady side of its neighbour appears green or dark by contrast. Again, observe the criss-cross shadows under a shrub scantily dressed with leaves, as typical of dry tropical countries.

My contention is that light influences the distribution of pigment in the skin. The primitive pattern is one of longitudinal stripes, and at least some of these are intimately connected with the distribution of primitive blood-vessels, *e.g.*, the so-called epigastric veins. How a few stripes can give rise to more is easily observed: the pigment in the intervening dark bands is not evenly distributed, but collects near the margins, the centre becomes lighter and ultimately the uniform band is transformed into two dark and one new light stripe. This is a common phenomenon in lizards, *cf.*, *C. deppei* and Werner.\* The production of a white band by confluence of white spots which have appeared in a dark field, is fundamentally the same process, *cf.* *Ameiva* and Werner fig. 58. Longitudinal stripes then, being referable to the preformed course of blood-vessels; are natural, and we can imagine how they are emphasised or stimulated by the skin being continuously submitted to linear lights and shades. The foundation for their direction was laid by the blood-vessels; oblique markings are out of the question in bilateral creatures, but transverse markings are quite possible, even to be expected, but they cannot be produced directly out of longitudinal lines. These have first to be broken up and the fragments have to be recombined. This is

\* "Untersuchungen über die Zeichnung der Wirbelthiere," 'Zool. Jahrb., Syst.' VI. (1892), p. 155—229, Plates 6—10; in particular, Plate 9, figs. 44 and 45.

exactly the process which we observe in these lizards. Why are the continuous lines broken, and why do secondary spots appear in the intermediate fields? Because the epigastric and cardinal veins are superseded by intercostal, *i.e.*, transverse vessels, and the linear disposal of pigment is incessantly interfered with by the shadows and lights of the living, therefore moving animal. And it is infinitely more natural that these shadows and lights will fall cross-ways upon a cylindrical body than lengthwise. It may be a mere coincidence, but it seems significant that longitudinal stripes are the prevalent pattern mostly in small species, and that to take one of our cases, *C. mexicanus* loses these stripes when it passes beyond the size of *C. sexlineatus* or *C. deppei*.

Next comes the question why do any of these lizards retain their stripes if it is the natural course of onward evolution to lose them? The answer can only be that small-bodied lizards, living amongst sparse tufts of grass have their pattern less interfered with than larger species, that the linear marking is even enhanced by the distribution of light, and last, not least, that natural selection raises no objection to such a case of epistasis. If these should afford protective advantages, then it will be all the more likely that communities of individuals, wherever they happen to live under the same conditions, will consolidate themselves into the same kind of race, and if there are also "structural" changes, then the systematist will condescend to call them sub-species, or even species.

This brings us to a consideration of the structural variations mentioned on pp. 111 and 112. These variations neither go together nor with the evolution of the colour-pattern. One individual may have reached perfection in the matter of femoral scales, and in colouration, while it lags behind in other features, and *vice versa*, in kaleidoscopic, endless combinations and permutations. For some of these modifications we can at least imagine their use. For instance, the protective advantage of the plates, enlarged in size and in numbers, which encase those surfaces of the limbs which come into contact with obstructions like thorny undergrowth, sharp blades of grass, &c. The collar, and the rest of enlarged scales on the middle of the throat, may be in relation to the mode of pouncing upon their prey, and rushing through obstructions.

But, after all, the detail of these variations presents such minute differences that immediate advantage, or weeding out, is out of the question. The fact remains that individuals of *C. guttatus*, possessed of only 20 femoral pores, grow up to propagate the species in exactly the same locality as those which can boast of 25 pores, and have 7 instead of 11 or 12 rows of femoral plates. Where can be the disadvantage of the retention of a few minute granules between the larger collar-  
as described in *C. deppei*? The same applies to the minute of the colour-pattern. There are specimens of *C. deppei*, with

8, 9, 10—11 stripes, all adult and breeding within a radius of a few hundred yards, living under the same conditions, exposed to the same enemies, namely, snakes and birds, which certainly cannot appreciate the difference of one stripe more or less.

Then there is the fact that some of the species pass, during their individual life, from 6 stripes to a livery with vanishing stripes, and with pale spots preponderant, and lastly to a cross-barred pattern of a totally different colour. Here we cannot apply the principle of the survival of the fittest, due to weeding out of those of the first year's lizards which do not happen to be striped, and those of the second year which do not happen to become spotted, and those of older age which do not manage to assume the cross-barred pattern. There are no young *C. mexicanus* which are not striped, but there exist in the same place sexually ripe specimens which present all the changes intermediate between Stages C and D, cf. p. 116.

The secret how they manage to survive is that they take care of themselves. I can assert positively that the young and the adult of *C. mexicanus* have different habits. They frequent open ground, where the vegetation is scarce enough not to impede their running about. A small lizard cannot run as fast as a large one which darts and bounds away like an arrow. The young remain in the open and when disturbed, after running a few yards, hide in their holes, or under stones, or if the worst comes to the worst, they hide between a few blades of grass which, with its strongly contrasting lights and shades, conceals them sufficiently. The larger specimens dart away at a furious pace, and make for the nearest hedge, shrub or bush, which may be 50 yards off; there they abide, not squatting, but in a semi-erect position with their eyes upon the enemy, under the criss-cross shadows, on the reddish grey ground and dry leaves.

But we cannot imagine such a complicated concatenation which implies the coming to grief of all those specimens, which at a certain size or age do not happen to possess the requisite equipment. Which are their enemies? Snakes and a few birds. The turkey-buzzard and the "road-runner," a ground-cuckoo, are entirely guided by the eye. The snakes hunt by sight and scent, but they do not seize their prey unless it moves, and I am not prepared to attribute to them much appreciation of colour, which, besides, is of no avail during the night, the chief hunting time of those snakes whose prey lives on the ground.

Lizards have often been used as illustrations of sexual selection. The colours of the males are certainly often striking and well displayed, but strong pigmentation is frequently relegated to the underparts, where they are not seen; for instance, the blue or the black on the belly of *C. deppiei*. It appears with the pairing season when metabolism is at its greatest activity, and, be it added, when it is also most upset



out of its normal course. But this colour increases in extent and intensity for a long time after the pairing, when the females are big with ripe eggs. Often the pigment is invisible externally, but it is nevertheless present in great quantities in the deeper strata of the skin, for instance, in *C. mexicanus* of both sexes. Sometimes the whole peritoneum and other cavities are jet black. The abundance of these waste products is stowed away where it cannot do any harm; such a favourite place are the underparts of lizards, and it is quite conceivable that natural weeding out takes place wherever the heaping up of such surplus pigment on the visible parts would upset an existing pattern which has turned out extremely advantageous. But this does not mean that selection has caused this pattern.

A feature well started, whether by internal or by external causes, is likely to proceed onwards with cumulative effect. Whatever it may be that has first guided pigment to be arranged in longitudinal lines, will continue to do so until a linear marshalling of pigment in the skin becomes an integral, almost ineradicable habit in that kind of organism. But size and proportions change with growth, blood-vessels yield to new systems of supply, new modes of distribution of light and colour follow with changes in the surroundings, and all these new conditions may make it not only difficult to keep up the old working of the organism but may even introduce new features, or improved methods.

Some lizards cannot keep their stripes unless they live in stripe-exciting surroundings; just as little can others keep pale spots in a desert. When spots are indicated in a desert creature, the spots are dark on a light ground; in the inhabitants of forests light spots on dark ground are the fashion.

An illustration of incidental advantage of features which are primarily due to constitutional conditions is the following. In lizards with very minute granular scales, e.g., *C. leppai*, the striation and colour of the back appear most vividly marked when the creature is seen from behind, but if looked at from the head tailwards, our eye more or less in level with the long axis, then the lizard assumes an almost stripeless and neutral tint. This latter phenomenon may be useful to the lizard in the pursuit of its prey, just as much as the striation may be advantageous in saving its own skin whilst running away from, and dazzling its pursuer. This phenomenon results from the fact that all scales, even the minutest, are more or less imbricating.

To appreciate these effects of colour and pattern, it is as well to mention, that we must contrive to look at these creatures from their own perspective, in their own level, not from a bird's-eye view. For instance, when lying on the ground ourselves, we appreciate the concealing, or dazzling effect of the lateral spots which are such a common feature in male ground-lizards; and we also observe that their more sombre-coloured females get on just as well without these "orna-



**FIG. 2.** *C. striatus.*





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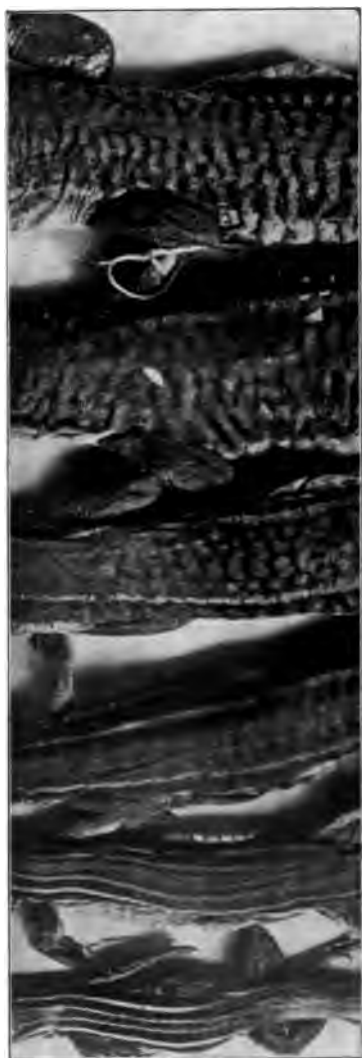
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FIG. 4. *C. mexicanus*.



1000

ments" as which we rashly interpret these and similar distributions of colour.

What we see as the individually variable detail is the outcome of the yielding of the organisms to physical circumstances; and the tendency to reproduce what its ancestors have become possessed of through these same stimuli, enhances, accumulates, quickens the same effect. Some lag behind, or never attain, what for the present may be the highest stage. Others are born ready, and during their life proceed further along the well-established lines and step even beyond the normal stage. That this in time will be superseded is only a question of time.

This kind of variation, when the various degrees of instances can be arranged in continuous lines which themselves coincide with a morphological sequence, I have termed *orthogenetic*.

#### DESCRIPTION OF THE PLATES.

##### PLATE 3.

FIG. 1.—*Cnemidophorus deppei*, nat. size. Three first specimens on the left with 9 white stripes; the fourth and fifth with 10; the sixth and seventh with 11; the last on the right with 8 stripes.

FIG. 2.—*C. striatus*,  $\frac{3}{4}$  nat. size. The first specimen on the left illustrates stage A; the second stage D, the third stage B, the rest stage C.

##### PLATE 4.

FIG. 3.—*C. guttatus*, nat. size.

FIG. 4.—*C. mexicanus*, nat. size. Youngest specimen on the left, oldest on the right side.

##### PLATE 5.

FIG. 5.—*C. bocourti*,  $\frac{3}{4}$  nat. size.

FIG. 6.—*Ameiva undulata*,  $\frac{3}{4}$  nat. size. Three specimens on the left are females, the fourth is an immature, the others are adult males.

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"Upon the Bactericidal Action of some Ultra-violet Radiations as Produced by the Continuous-Current Arc." By J. E. BARNARD and H. de R. MORGAN. Communicated by Sir HENRY ROSCOE, F.R.S. Received June 15,—Read June 18, 1903.

(From the Jenner Institute of Preventive Medicine.)

The experiments here described have been carried out with the object of determining the effect on the vitality of bacteria, as the result of exposure to the arc spectra of carbon and of various metals.

The organisms experimented with have been the *Bacillus coli communis*, *B. prodigiosus*, *B. subtilis*, *Micrococcus tetragenus*, *Staphylococcus aureus* and *Bacillus tuberculosis*.

The spectroscope was provided with quartz lenses and prism, and a subsidiary quartz lens of 18-inch focus was used to project the image of the arc on to the slit. The instrument was adjusted as for photography, except that the slit was somewhat more open than is generally the case for that purpose. The method of experimenting was to project the spectrum on to an agar film, contained in an ordinary Petri dish, over the surface of which had been spread with a sterilised brush an active culture of one of the organisms mentioned. The plates were exposed to the light directly after inoculation and were then incubated for 24 hours at 37° C. The part of the plate on which no portion of the spectrum was allowed to fall grew normally and served as a control.

It was found that the bactericidal action was entirely confined to the ultra-violet region. With the spectrum projected as described, the results were as follows :—

| Current.    | Width of slit. | Length<br>of exposure. |                                                                                |
|-------------|----------------|------------------------|--------------------------------------------------------------------------------|
| 11 ampères. | 0·5 mm.        | 15 mins.               | Effect slight, but bands discernible.                                          |
| 11     ,,   | 0·5     ,,     | 20     ,,              | Effect well marked.                                                            |
| 11     ,,   | 0·5     ,,     | 45     ,,              | Effect very marked, so that the bands almost merged and formed a sterile area. |

With exposures as long as two hours no effect whatever was obtained in any other portion of the spectrum, even when the slit of the spectroscope was opened to an extent which in photographing would have been regarded as inadmissible. The active radiations lie in that portion of the spectrum between wave-length 3287 and 2265. The wave-lengths were determined by reference to the arc spectrum of

cadmium. Visually the lines in the ultra-violet region can be observed by projecting the spectrum on to a fluorescent screen of sulphate of quinine. We, however, obtained photographs of the cadmium spectrum under precisely the same conditions as those under which the bacterial plates were obtained, and were thus able to identify the lines occurring in the photograph, with those on the bacterial plates. As these lines are known, their wave-length is at once obtained by comparing the photographs with a chart on which the wave-lengths are indicated. The photographic method, therefore, reduces the chance of mistakes which might arise from personal error in observation. It, therefore, appears that relatively the action of other portions of the spectrum is negligible compared with the activity of this portion, although it is probable that when using white light there is a slight action which extends over the whole spectrum. Neither the extreme ultra-violet rays nor those nearest to the visible violet appear to be active. The affected portion of the bacterial plates corresponded with a photograph taken of that portion of the spectrum, and it was possible to identify the nearly sterile lines on the plates with those known to exist in the ultra-violet spectrum of carbon.

In view of this result we were led to experiment with the arc spectra of various metals, such as iron, cadmium, silver and aluminium. The results with these entirely agreed with those obtained with carbon, except that the action is greater in proportion to the number and intensity of the lines occurring in what we may call the bactericidal region.

It, therefore, appeared that an electrode composed entirely or partly of iron, should be more actively bactericidal than a carbon one, and this we found to be the case. A convenient form we found to be one in which in the case of the positive electrode, we removed the soft carbon core and substituted for it a mixture consisting of the particular metal desired and sufficient carbon, in the form of sugar, to prevent the core from dropping out. Using a positive electrode so prepared and an ordinary carbon negative electrode, the effect on *Bacillus coli communis* contained in a hanging drop was as follows:—

Distance of hanging drop from arc, 10 cm. Current used 11 ampères.

| Ordinary carbons ..... | Organisms killed in 30 mins. |   |      |
|------------------------|------------------------------|---|------|
| Iron           " ..... | "                            | " | 15 " |
| Cadmium     " .....    | "                            | " | 15 " |
| Aluminium   " .....    | "                            | " | 25 " |

The organisms were proved to be killed by failure to obtain sub-cultures, but the motility was arrested long before the death of the organism.

The light was allowed to pass through a metal cylinder, closed at



each end with a disc of quartz, and through which water was kept circulating to absorb heat rays. The slide on which the hanging-drop cover slip was placed was made of quartz to avoid interception of the ultra-violet rays. The hanging drop thus mounted was then placed on this water-circulating apparatus and the light from the arc was projected through from below upwards, so as to pass through the water and the quartz slide on to the hanging drop.

We have been unable to find that any of the radiations contained in the spectrum are penetrative to organic substances such as agar, or dead animal or vegetable tissue. Neither can they penetrate living tissues, but we are continuing experiments in this direction to more exactly determine their action.

The conclusion to be drawn, therefore, is that the bactericidal action of light is almost entirely due to the action of those radiations in the ultra-violet region of the spectrum which are included between the wave-lengths 3287 and 2265. It is, therefore, necessary that any source of light used as a bactericidal agent should be rich in these rays.

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“On the Propagation of Tremors over the Surface of an Elastic Solid.” By HORACE LAMB, F.R.S. Received June 11,—Read June 11, 1903.

(Abstract.)

The paper treats of the propagation of vibrations over the surface of a “semi-infinite” isotropic elastic solid, *i.e.*, a solid bounded only by a plane. For purposes of description, this plane may be conceived as horizontal and the solid as lying below it, although gravity is not specially taken into account.

The vibrations are supposed due to an arbitrary application of force at a point. In the problem most fully discussed this force consists of an impulse applied normally to the surface; but some other cases, including that of an internal source of disturbance, are also (more briefly) considered. Owing to the complexity of the problem, attention has been concentrated for the present on the vibrations as they manifest themselves at the free surface; the modifications which the latter introduces into the character of the waves propagated into the interior have accordingly not been examined minutely.

The investigation may perhaps claim some interest on theoretical grounds, and also in relation to the phenomena of earthquakes. Writers on seismology have naturally endeavoured, from time to time, to interpret the phenomena, at all events in their broader features, by the light of elastic theory. Most of these attempts have been based

on the general laws of wave-propagation in an unlimited medium, as developed by Green and Stokes; but Lord Rayleigh's discovery\* of a special type of surface-waves has made it evident that the influence of the free surface in modifying the character of the vibrations is more definite, and more serious, than had been suspected. The present memoir seeks to take a further step in the adaptation of the theory to the actual conditions, by investigating cases of *forced* waves, and by abandoning (ultimately) the restriction to simple-harmonic vibrations. Although the circumstances of actual earthquakes must differ greatly from the highly idealised state of things which we are obliged to assume as a basis of calculation, it is hoped that the solution of the problems here considered may not be altogether irrelevant.

It is found that the surface disturbance produced by a single impulse of short duration may be analysed roughly into two parts, which we may distinguish as the "minor tremor" and the "main shock," respectively. The minor tremor sets in at any place, with some abruptness, after an interval equal to the time which a wave of longitudinal displacement (in an unlimited medium) would take to traverse the distance from the source. Except for certain marked features at the inception, and again (to a lesser extent) at an epoch corresponding to that of direct arrival of transversal waves, it may be described, in general terms, as consisting of a long undulation leading up to the main shock, and dying out gradually after this has passed. Its time-scale is more and more protracted, and its amplitude more and more diminished, the greater the distance from the source. The main shock, on the other hand, is propagated as a solitary wave (with one maximum and one minimum, in both the horizontal and vertical displacements); its time-scale is constant, and its amplitude diminishes only in accordance with the usual law of annular divergence, so that its total energy, unlike that of the minor tremor, is maintained undiminished. Its velocity is that of free Rayleigh waves, and is accordingly somewhat less than that of waves of transversal displacement in an unlimited medium.†

The paper includes a number of subsidiary results. The various problems are attacked, in the first instance, in their two-dimensional forms. The interpretation of the analytical results is then com-

\* 'Lond. Math. Soc. Proc.' vol. 17, p. 4 (1885); 'Scientific Papers,' vol. 2, p. 441.

† Compare the concluding passage of Lord Rayleigh's paper:

"It is not improbable that the surface-waves here investigated play an important part in earthquakes and in the collision of elastic solids. Diverging in two dimensions only, they must acquire at a great distance from the source a continually increasing preponderance."

The calculations show that the preponderance is much greater than would be inferred from a mere comparison of the ordinary laws of two-dimensional and three-dimensional divergence.

paratively easy; and it is found that a good deal of the work can be utilised afterwards in the transition to the three-dimensional cases. Again, the investigation of a simple-harmonic source of disturbance is a natural preliminary to that of a source varying according to an arbitrary law.

Incidentally, new solutions are given of the well-known problems where a periodic force acts transversally to a line, or at a point, in an unlimited solid. These serve, to some extent, as tests of the analytical method, which presents some features of intricacy.

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"Some Preliminary Observations on the Assimilation of Carbon Monoxide by Green Plants." By W. B. BOTTOMLEY, Professor of Botany, King's College, London, and HERBERT JACKSON, Assistant Professor of Chemistry, King's College, London. Communicated by Professor J. REYNOLDS GREEN, Sc.D., F.R.S. Received June 11,—Read June 18, 1903.

During an investigation by one of us some years ago on "Carbon Monoxide in some of its Physiological Effects," a few experiments were made on plants, and it was noticed that a hyacinth, which had commenced growth and was showing a few small leaves, continued to grow for some weeks when placed in a bell jar in which the air had been replaced by a mixture of 80 per cent. of carbon monoxide and 20 per cent. of oxygen. As this was contrary to the usually accepted ideas as to growth of green plants in carbon monoxide, a number of experiments were recently commenced with a view to determining how far carbon monoxide could replace carbon dioxide as a source of carbon supply for green plants. Although the hyacinth grew in carbon monoxide the experiment was not considered conclusive, because of the large stores of carbohydrates in the bulb. Young plants of *Tropæolum majus*, grown in sterilised sand and supplied with a nutritive solution free from all traces of carbonates, were therefore used. It was found that *Tropæolum* plants would not grow in air in which the carbon dioxide had been replaced by an equal quantity of carbon monoxide. When, however, the relative solubilities of the two oxides of carbon in water were taken into account, and the amount of carbon monoxide was increased proportionately—about twenty times as much carbon monoxide as carbon dioxide—the plants grew well, being healthy and normal. Experiments were also made with varying proportions of carbon monoxide in air free from all traces of carbon dioxide. The plants grew freely and well in proportions varying from 1 to 70 per cent. of carbon monoxide, when care was taken that as the higher percentages of carbon monoxide

were reached, oxygen was added so as to keep the amount of this gas approximately equal to that in normal air.

One very significant fact was noticed during the experiments. When in bright sunshine a negative pressure was always observed in the bell jars containing plants growing in carbon monoxide. This result tends to confirm Baeyer's theory of photosynthesis. In normal photosynthesis the volume of oxygen given off is equal to the volume of carbon dioxide undergoing decomposition. If, however, carbon monoxide be used directly by the plant, only half the amount of oxygen would be given off, hence the negative pressure.

Experiments were also made to find if starch was formed in plants growing in carbon monoxide. *Tropeolum* plants growing in water culture solution were placed in the dark for 48 hours, when the leaves were shown by the iodine test to be free from starch. Some of the plants were then placed in air free from carbon dioxide; others in carbon dioxide free air, but containing 10 per cent. of carbon monoxide. All were then exposed to sunlight for three days, and again examined for starch. The plants grown in carbon dioxide free air had formed no starch, whilst those grown in carbon monoxide gave the iodine test most markedly. Sections of the green stems showed quantities of starch grains in the ground tissue, especially crowded around the vascular bundles, in the plants grown in carbon monoxide, but none in those grown in carbon free air.

Experiments on the germination and growth of seeds in carbon monoxide also gave satisfactory results. Seeds of *Lepidium sativum* were planted in sterilised sand and placed in a mixture of 65 per cent. carbon monoxide and 35 per cent. oxygen. The seeds germinated and formed healthy plants, growing quite normally for three weeks. Certain preliminary determinations of the amount of carbon in the seeds and in the plants point to the accumulation of organic carbon, and as the only possible source for this increase of carbon is the carbon monoxide, some of it must have been assimilated. These results are so important and the results so striking that it has been thought advisable to repeat the determinations with new and specially devised apparatus before quoting figures. Also it is intended to carry out further experiments with carbon monoxide, and with compounds in which the CO-group exists in combination.

In all these experiments with carbon monoxide, great care was taken that efficient absorbers of carbon dioxide were used, and the pressure in the bell jars was regulated by potash-sealed valves.

The present communication is only a note to indicate the general bearings of the research, and does not give any account of many experiments and observations of interest which the authors hope to give later in a detailed paper.

"The Forces Acting on a Charged Condenser moving through Space." By Professor F. T. TROUTON, F.R.S., and H. R. NOBLE, B.Sc., University College, London. Received June 11,—  
Read June 18, 1903.

(Abstract.)

If a charged condenser be placed with its plane in the direction of the æther drift, then on the assumption that a moving charge develops a magnetic field, there will be associated with the condenser a magnetic field perpendicular to the lines of electric induction, and to the direction of the motion. If  $N$  be the electrostatic energy of the condenser, the magnetic energy produced when moving with velocity  $w$  through the æther with its plates parallel to the motion is  $N (w/v)^2$ , where  $v$  is the usual velocity of propagation. But when the plates of the condenser are perpendicular to the direction of motion, the effects of the opposite charges will neutralise each other, and there will be no magnetic field produced. Thus if we have a condenser freely suspended with its plates making an angle  $\psi$  with the direction of the æther drift, the magnetic energy is  $N (w/v)^2 \cos^2 \psi$ . The couple tending to increase  $\psi$  is  $-dE/d\psi$ , which is  $N (w/v)^2 \sin 2\psi$ . By utilising the Earth's motion through space, we can arrange (generally) the experiment so that  $\psi = 45^\circ$  and  $w$  is the total velocity of the Earth through space. The couple is then a maximum equal to  $10^{-8} N$  for the orbital velocity alone, and to  $2.3 \times 10^{-8} N$  when we include the Sun's proper motion.

A condenser was suspended by a fine wire and charged. The charges were let into the plates of the condenser by means of this suspending wire, and by a wire which hung from beneath dipping into a liquid terminal. Observations were made at different times in the day when the plane of the condenser made various angles with the direction of the drift.

The final form of the apparatus is as follows:—The suspension is a phosphor bronze strip 37 cm. long, the finest that could be obtained. This was soldered at its lower end A to a copper cap, fixed to the condenser protecting the projecting tin foil tags and making contact with them by means of fusible metal. The upper end of the suspension was wound on a small windlass which was insulated by a mica plate fixed to an annular wooden ring, forming the lid to the inner zinc vessel. A small glass bell jar covered the windlass, contact being made by a wire passing through the small cork at the top. A small brass tube shields the upper part of the suspension, and a thin metal cylinder protects the point of support. The condenser is inserted in a celluloid ball, to diminish the effect of convection currents. Two cylindrical zinc vessels protect the apparatus, the interspace being

packed with cotton wool; these were earthed together with the ball containing the condenser. A plane mirror was attached to the condenser, this was viewed by means of a telescope and scale, through small mica windows in the zinc coverings. The potential was maintained by a Wimshurst machine, to the terminals of which was attached a Kelvin-White voltmeter.

The best conditions under which to make the experiment are calculated. These include considerations as to the time of day and time of year, and azimuth of the plane of the condenser. This calculation is made for both the orbital motion and the proper motion of the solar system.

The following table gives the final results obtained. These were observations taken after many months of experience with the apparatus and were considered by us as conclusive against there being any such effect as we were seeking :—

| Date.   | Time.       | Potential<br>in volts. | Deflection<br>calculated<br>(annual<br>motion). | Deflection<br>calculated<br>(annual +<br>proper). | Deflection<br>observed. |
|---------|-------------|------------------------|-------------------------------------------------|---------------------------------------------------|-------------------------|
|         |             |                        | cm.                                             | cm.                                               | cm.                     |
| March 9 | 12. 15 P.M. | 2100                   | -2.6                                            | -6.8                                              | -0.35                   |
| " "     | 6. 0 "      | "                      | +0.8                                            | 0                                                 | -0.12                   |
| " 10    | 12. 0 (day) | "                      | -2.6                                            | -6.8                                              | -0.34                   |
| " "     | 3. 0 P.M.   | "                      | -1.2                                            | -3.4                                              | -0.23                   |
| " "     | 6. 0 "      | "                      | +0.8                                            | 0                                                 | -0.26                   |
| " 12    | 12. 0 (day) | "                      | -2.6                                            | -6.8                                              | -0.36                   |
| " "     | 3. 0 P.M.   | "                      | -1.2                                            | -3.4                                              | -0.25                   |
| " "     | 6. 0 "      | "                      | +0.8                                            | 0                                                 | -0.32                   |
| " 13    | 5. 30 "     | "                      | +0.8                                            | 0                                                 | -0.34                   |
| " "     | 6. 30 "     | "                      | +0.8                                            | 0                                                 | -0.18                   |
| " 18    | 3. 0 "      | 2000                   | -1.2                                            | -3.4                                              | -0.02                   |

The largest observed deflection 0.36 cm. barely exceeds 5 per cent. of the calculated deflection 6.8 cm.

There are also other observations on the electrostatic effects to show that the deflection observed was a purely capricious action and could in no way be attributed to the relative motion of the earth and the æther.

There is no doubt that the result is a purely negative one, as in other cases of possible interaction between æther and matter that have been examined. As the energy of the magnetic field, if it exists (and from our point of view we must suppose it does) must come from somewhere, we are driven to the conclusion that the electrostatic energy of a charged condenser must diminish by the compensating amount  $N(u/v)^2$ , where  $N$  is the electrostatic energy, when moving with a velocity  $u$  at right angles to its electrostatic lines of force.

"On the Synthesis of Fats accompanying Absorption from the Intestine." By BENJAMIN MOORE, M.A., D.Sc., Johnston Professor of Bio-chemistry at University College, Liverpool. Communicated by Professor C. S. SHERRINGTON, F.R.S. Received June 15,—Read June 18, 1903.

(From the Physiological Laboratory, University College, Liverpool.)

The experiments here recorded form a continuation of work previously carried out by the author in conjunction with D. P. Rockwood\* and with W. H. Parker.†

In the earlier papers it was shown that the bile possesses solvent properties for both free fatty acids and soaps, which taken in conjunction with the hydrolytic action of the pancreatic juice upon fats renders the view highly probable that all the fats of the food are absorbed, not as an emulsion but in soluble form as fatty acids and soaps. Such a view yields an easy explanation of the conjoint action of the bile and pancreatic juice in fat absorption, and of the defective uptake of fat when either fluid is absent from the intestine.

It also supplies an important function for the bile, and explains why the circulation of the biliary acids occurs.

These results have since been confirmed and in certain respects extended by Pflüger‡, who also supports the view that all the fat of the food is taken up from the intestine in soluble form.

The experiments described in this present communication were designed chiefly with the object of studying the subsequent changes which take place in these absorbed soluble constituents of fat digestion.

It is known from the experiments of Munk§ that, even when free fatty acids are taken in as food, neutral fat is the chief fatty constituent present in the lymph of the thoracic duct, and this is also the case when neutral fat is being taken up from the intestine.

This observation clearly demonstrates that the fatty acids and soaps formed in the intestine are synthesized back into neutral fat before the thoracic duct is reached, but no clear experimental proof is in existence as to where along the channel of absorption this synthesis occurs, nor in what manner it takes place, that is to say, as to whether it is carried out by an intracellular enzyme, or is dependent on and inseparable from cells lying somewhere along the path of absorption.

\* 'Roy. Soc. Proc.,' vol. 60, 1897, p. 438; 'Journ. of Physiology,' vol. 21, 1897, p. 58.

† 'Roy. Soc. Proc.,' vol. 68, 1901, p. 64.

‡ 'Arch. f. die ges. Physiologie,' vol. 82, 1900, pp. 303, 381; vol. 85, 1901, p. 1; vol. 88, 1902, pp. 299, 431; vol. 90, 1902, p. 1.

§ 'Virchow's Arch.,' vol. 80, 1880, p. 17; vol. 95, 1884, p. 452.

It is true that the change is currently believed to take place in the columnar cells of the intestine, but a review of the experimental evidence on which this statement rests will suffice to show that the proof is incomplete, and hence the subject has here been more rigorously investigated.

The chief facts for the view that the synthesis occurs in the intestine are, the histological appearance presented by the columnar cells when taken during fat absorption and examined by the usual micro-chemical tests for fats; secondly, the naked-eye appearance of the mesenteric lacteals and microscopic examination of their contents during fat absorption; and, thirdly, the supposed action of extracts of intestinal mucous membrane in synthesizing, *in vitro*, neutral fats from solutions of soap and glycerine.

The objections to these supposed proofs are, that the histological and naked-eye appearances taken to be characteristic of fat in the columnar cells and mesenteric lacteals might equally well be given by free fatty acid in suspension, and hence supply no proof of a synthesis of neutral fat, since no chemical examination of the fatty matters present at these stages in fat absorption have hitherto been made so far as the author is aware. In the second place, the proofs given of the synthesis of neutral fat *in vitro* from soap and glycerine by intestinal cells are based upon incomplete analyses, and, as will be shown later, are erroneous.

It may be stated at once, however, that the present investigation has shown that the synthesis does occur in the intestinal mucosa, or, to put the matter more rigorously, before the mesenteric lacteals have been reached, but that it has been impossible to imitate this action *in vitro* either by detached cells or cell-free extracts.

There are two places along the path of the absorbed fatty material from intestine to thoracic duct at which the lymph comes into intimate relationship with cells, and at which accordingly chemical changes might be expected to occur. These situations are the intestinal villus and the mesenteric lymphatic gland, and the experimental method of procedure suggests itself of examining the chemical composition of the fatty matter in these situations, and before and after passing through them. This method has been employed in the present investigation, and in so doing the percentage of neutral fat and of free fatty acids have both been directly determined in ethereal extracts of the intestinal mucosa, and lymph of the mesenteric lymphatic vessels obtained during fat absorption.

The lymph in the mesenteric lacteals during fat absorption has not previously been examined chemically as to its content in neutral fat and free fatty acid, probably from the difficulty experienced in collecting it in sufficient quantity from the exceedingly narrow vessels.



It is difficult to wash the intestinal mucous membrane free from attached globules of fat which lie between the villi, and hence to be certain that all the fat submitted to analysis has been obtained from the interior of the villi and columnar cells, and so the results recorded below cannot be taken as quantitatively accurate although they do undoubtedly show that a considerable amount of synthesis has occurred in the villi, and that the synthesis is in progress and not in that state of completion which is found in the lymph of the mesenteric lacteals.

It is hence fortunate that it was found possible to obtain lymph from the small mesenteric lymph vessels in sufficient quantity to make analyses of both neutral fat and free fatty acid, and so prove conclusively that the latter is practically absent by the time the lymph is leaving the intestinal wall.

It was found quite impossible to introduce a cannula into these lymphatic vessels, and hence the lymph was obtained by cleansing the mesenteric surface, opening the lymphatic with a fine pointed pair of scissors, carefully avoiding accompanying blood vessels, and allowing the lymph to escape on to the mesenteric surface. The fluid was then collected in wide capillary tubes, by capillarity or suction, until a sufficient amount had been obtained for the necessary analyses.

A second method of investigating the action of the various cells which the lymph, containing the fatty constituents, encounters on its path of absorption, is to prepare these tissues, or extracts of them free from cells, and test *in vitro* whether such preparations exert any synthetic action.

This method was also employed with extracts of intestinal mucous membrane and lymphatic glands, and as the results differed essentially from those of previous observers who had used this method, but without making so complete analyses of the supposed synthesized products, pancreatic extracts were also similarly tested.

Since it was also thought that the absence of synthesis of neutral fat shown by the experiments might be due to the lack of a supply of energy by the cells or enzymes contained in them, an attempt was made in a certain number of the experiments to supply a source of energy by the addition of glucose to the soap and glycerine of the other experiments. But here also the result remained negative and it may be stated that throughout no appreciable synthesis of neutral fat from its constituents was ever obtained.

One positive result observed, which does possess a certain degree of physiological importance, was that all three types of extract, but especially that of the pancreas, possess a marked power of setting free fatty acid from the soap employed.

A protective action would be exercised in the body in this manner against the appearance of the highly poisonous soaps in the circulation.

C. A. Ewald\* was the first observer who stated that the fresh mucous membrane of the small intestine is capable *in vitro* of synthesizing neutral fat from a mixed solution of soap and glycerine, and recently Hamburger† has published a similar result obtained with the mucous membrane of the large intestine. Both the above observers, however, relied upon the difference in weight between the total ethereal extract, and the weight of fatty acid, as shown by titration with standard alkali, of the ethereal extract, for giving the amount of neutral fat, and did not make direct determinations by saponification with caustic alkali of the amount of neutral fat. Here it is believed by the present writer that they fell into an error, for had such an indirect method been used in the experiments recorded below, similar results to those of Ewald and of Hamburger would have been obtained in many cases. The direct determination by saponification shows, however, that the difference between total ethereal extract and free fatty acid is due not to neutral fat, but to soap dissolved by the ether.‡

Other observers have described synthesis, by extracts of intestinal mucous membrane, and several other tissue extracts, of such esters as ethyl-butyrate,§ and monobutyryn,|| but no detailed account of these experiments need be given since the conditions of synthesis and hydrolysis of such esters are probably widely different from those applying to the triglycerides.¶

*I.—Experiments on the composition of the lymph of the mesenteric lymphatic vessels during fat absorption.*

The lymph was obtained by the method described above from the lacteals of anæsthetised dogs, at a period of 5—7 hours, subsequent to feeding on olive oil.

The ethereal extract obtained from the lymph was evaporated to dryness, dissolved in hot alcohol and titrated with decinormal sodic hydrate solution using phenol-phthalein as an indicator.

From the amount of standard sodic hydrate used the percentage of free fatty acid in the ethereal extract was calculated.

\* 'Arch. f. Physiol. u. Anat., Physiol. Abth.,' Suppt. vol., 1883, p. 302.

† 'Arch. f. Physiol.,' 1900, p. 433.

‡ Hamburger attempted in his experiments to remove such a source of error, by making a control to which soap was added after digestion, but the amount of soap dissolved appears to vary so as to make this procedure ineffectual, and reliable results can only be obtained by a direct estimation by saponification of the neutral fat.

§ Kastle and Loevenhart, 'American Chemical Journal,' 1900, vol. 24, p. 491; Loevenhart, 'American Journal of Physiology,' 1902, vol. 6, p. 331.

|| Hanriot, 'Comptes rendus de la Société de biologie,' 1901, p. 70.

¶ See Lewkowitsch, 'Journal of Society of Chemical Industry,' 1903, vol. 22 No. 2.

The neutral alcoholic solution thus obtained was next evaporated down to a small volume, a measured volume (usually 10 cc.) of standard alcoholic potash solution was added, and the mixture boiled for 20—30 minutes, in a small flask fitted with a reflux tube, in order to insure complete saponification of all the neutral fat present.\* Finally the contents of the flask were accurately neutralised by standard hydrochloric acid, with phenol-phthaleïn as indicator. The difference in value between alkali added before boiling and acid required afterwards then supplied the necessary *datum* for calculating the percentage of neutral fat.

*Expt. 1.*—A dog, weighing 12 kilos., was fed with 100 grammes of olive oil at 9.30 A.M. and anæsthetised at 3.30 P.M., when the lacteals were exposed, and seventeen drawn-out tubes were filled with milk-white chyle by opening the lacteals.

|                                    | Grammes. |
|------------------------------------|----------|
| Weight of lymph .....              | = 1.2990 |
| „ total ethereal extract..         | = 0.0618 |
| „ free fatty acid .....            | = 0.0028 |
| „ neutral fat .....                | = 0.0564 |
| Percentage of free fatty acid .... | = 4.7    |
| „ neutral fat .....                | = 95.3   |

*Expt. 2.*—Weight of dog = 8.6 kilos., fed with 50 grammes of olive oil at 9.30 A.M.; chyle collected as before at 4.30 P.M., and twenty-three tubes charged with the fluid.

The lymph was weighed and analysed with the following results:—

|                                    | Grammes. |
|------------------------------------|----------|
| Weight of lymph .....              | = 0.9550 |
| „ ethereal extract.....            | = 0.1052 |
| „ free fatty acid .....            | = 0.0042 |
| „ neutral fat .....                | = 0.1031 |
| Percentage of free fatty acid .... | = 3.9    |
| „ neutral fat .....                | = 96.1   |

*Expt. 3.*—Weight of dog = 12.4 kilos., fed at 9 A.M. with 100 grammes of olive oil; chyle collected at 3 P.M. by a fine pipette into a porcelain capsule, and then weighed and analysed.

|                                    | Grammes. |
|------------------------------------|----------|
| Weight of lymph .....              | = 1.8712 |
| „ ethereal extract.....            | = 0.1450 |
| „ free fatty acid .....            | = 0.0042 |
| „ neutral fat .....                | = 0.1326 |
| Percentage of free fatty acid .... | = 3.1    |
| „ neutral fat .....                | = 96.9   |

Hence in these experiments practically all the fatty matter (upwards of 95 per cent.) is present in neutral fat.

\* Köttstorfer's method, as described in Sutton's 'Volumetric Analysis,' 8th Ed., p. 402. Preliminary experiments to test the method with pure neutral olein gave practically theoretical values.

## II. *Experiments on the Composition of the Fatty Constituents present in the Intestinal Mucosa during Fat Absorption.*

The animals used in the previous set of experiments were killed immediately after the lymph had been collected, and the entire small intestine was removed, cut open longitudinally and thoroughly washed in running water to remove as completely as possible all adherent fat.

The intestine was next stretched out, mucous surface upward, upon a clean glass plate and the mucous membrane rubbed off with the back of a knife.

The pulpy mucous membrane thus obtained was weighed and extracted, first with a mixture of alcohol and ether (1 alcohol to 3 of ether) and then with ether alone.

The solvents were decanted off, the solutions mixed and evaporated to dryness. The dried residue was next extracted with dry ether, filtered, and the ethereal extract evaporated to dryness.

The residue was weighed, and in it the amount of free fatty acid and neutral fat were determined by the methods already described in connection with the previous series of experiments.

*Expt. 1.*—Total weight of moist mucous membrane = 31.7 grammes; weight of total ethereal extract = 1.1524 grammes; weight of free fatty acid = 0.1802 gramme; weight of neutral fat = 0.9722 gramme; percentage of free fatty acid = 15.7; percentage of neutral fat = 84.3.

*Expt. 2.*—Weight of moist mucous membrane = 14.4 grammes; weight of total ethereal extract = 0.8074 gramme; weight of free fatty acid = 0.2904 gramme; weight of neutral fat = 0.5303 gramme; percentage of free fatty acid = 35.4; percentage of neutral fat = 64.6.

In these experiments the percentage of free fatty acid is much higher than in the lymph of the mesenteric lacteals, showing that the process of synthesis is in progress, and not yet complete.

## III. *Experiments on the Action of Pancreatic, Lymphatic and Intestinal Cells, and of Cell-free Extracts of such Cells, upon Solutions of Soap and Glycerine.*

The tissues and extracts used in these experiments were obtained from the cat, dog, ox or pig, and similar effects were in all cases obtained.

In the case of the intestinal mucous membrane, the intestine taken from a freshly-killed animal was cut open longitudinally from end to end and then thoroughly washed either in a stream of running tap water or with 0.75 per cent. solution of sodium chloride.

It may be stated that no difference was ever found throughout the entire series of experiments in the action of extracts made with distilled water and those prepared with normal saline.

The mucosa was scraped off the inner surface of the intestine by rubbing with the back of a knife, and the soft uniform mass so obtained was gathered in a heap and chopped up on a glass plate. It was then transferred to a mortar and rubbed up alone or mixed with fine sand.

Portions were weighed out and treated with definite amounts of the extractives used, in an incubator at 36° C. for varying times.\*

When the action of the cells was to be tested, the ingredients to be acted upon were added when the cells were first placed in the incubator; but when cell-free extracts were to be tested, the tissue treated as above described was allowed to undergo previous digestion for a variable period. The extract was then filtered off, thoroughly centrifugalised, and the clear extract was used for the experiment.

In the case of the pancreas and abdominal lymphatic glands, the tissue was first finely minced and subsequently treated in similar fashion to the intestinal mucosa.

The strength of extract employed was not the same in all the experiments, and is stated in each individual case.

The soap used was sodium oleate prepared from pure olive oil. The oleic acid obtained by hydrolysis from this soap had a melting point of 17·5 C., and 0·214 grammes required 7·6 c.c. of  $\frac{1}{10}$  N caustic soda for neutralisation, the theoretical amount being 7·57 c.c.

### *Series A.*

*Expt. 1.*—Small intestine of cat during digestion of bread; no fat visible in lacteals, saline extract of 1 in 4, digested in incubator at 33° C. for 90 hours previous to addition of soap (2 per cent.) and glycerine (0·5 per cent.).

All the oleate dissolved, giving a clear solution; 1 hour later a few oily drops were visible in the solution under the microscope. Next morning (interval 17 hours 30 minutes) the fluid was yellow and cloudy like an emulsion, and some microscopic drops of fatty material were found floating on the surface of the fluid. Under the microscope a large number of oily globules of varying size were visible.

*Expt. 2.*—A like experiment on the abdominal lymphatic glands of the same animal, in saline extract of 1 in 5, same period of 90 hours previous digestion at 33° C. in incubator.

The extract, after centrifugalising, formed a clear reddish-yellow fluid in which no cellular elements were present when examined under the microscope; 10 c.c. of this fluid in a test-tube had 0·2 gramme of sodium oleate and 0·052 gramme of glycerine added, and the clear solution so obtained was heated in a water-bath to 38·5 C.

The experiment was commenced at 6 P.M., and next morning at 10.30 A.M. (interval = 16 hours 30 minutes) there was a thick yellow oily layer on the top

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\* During most of the experiments chloroform was added to prevent bacterial growth, but to make certain that cellular activity was not inhibited by the presence of the chloroform, in certain experiments it was not added, and in these experiments the extractions were made by previously boiled salt solution or water.

which formed a temporary emulsion on shaking, and the fluid, examined under a low power of the microscope, showed a field thickly studded over with highly refractile globules, closely resembling milk, as seen under the microscope.

The oily layer was removed by shaking up with successive quantities of ether, in which it was readily soluble, and after evaporation of the ether, the amount of ethereal extractive was weighed, and the percentage of free oleic acid in it was determined by titration with decinormal sodic hydrate, in warm alcoholic solution, using rosolic acid as indicator. It was found that 87·5 per cent. of the ethereal extract consisted of free oleic acid.

The lymphatic extract used was alkaline to rosolic acid and remained so during the reaction.

*Expt. 3.*—This experiment shows that the production of free acid from soap is not stopped by the prolonged action of sulphuretted hydrogen upon the tissue cells or extracts.

Fresh ox lymphatic glands were treated as above described, and then extracted in a flask, with 5 volumes of distilled water, which was saturated with sulphuretted hydrogen gas, and then tightly corked and kept in an incubator at 36° C. for 92 hours.

At the end of the interval the contents still had a strong odour of sulphuretted hydrogen. The fluid was separated from the tissue elements, and a water clear extract of a greenish-brown colour was obtained.

The fluid was charged again with sulphuretted hydrogen and left at room temperature, tightly corked for another 10 days. It was then filtered from a slight deposit of sulphur, and found to be slightly acid (acidity = 0·24 N). It was rendered alkaline (alkalinity = 0·02 N to rosolic acid) by excess of sodium carbonate.

A portion of 40 c.c. had 0·8 gramme sodium oleate and 0·4 gramme of glycerine added; the flask was saturated with sulphuretted hydrogen, corked and placed in the incubator at 36° C. for 24 hours when an oily layer had appeared on the surface. A single extraction with ether gave a residue weighing 0·355 gramme and containing 0·341 gramme of free oleic acid.

*Expt. 4.*—Cell-free extracts of the pancreas and small intestine (mucosa) of three cats, taken in condition of inanition, prepared as before, and digested with normal saline for a period of 43 hours in an incubator at 36° C. The solutions were made distinctly alkaline to phenol-phthalein, and the strengths were made equal to 1 in 9 of the fresh tissues.

Each extract (intestine and pancreas) was then measured out into four portions, each of 25 c.c., and the two sets of solutions were treated as follows:—

No. 1.—25 c.c. extract + 0·5 gramme oleate + 0·1 gramme dextrose + 0·16 gramme glycerine.

No. 2.—25 c.c. extract + 0·5 gramme oleate + 0·16 gramme glycerine.

No. 3.—25 c.c. extract + 0·5 gramme oleate.

No. 4.—25 c.c. extract + 0·5 gramme oleate + boiling before digestion.

The eight tubes were then placed in a water-bath at 36° C. and examined at intervals.

#### *Intestine.*

An examination 1½ hours after the commencement of the experiment showed turbidity in all four of the intestinal extract tubes, and under the microscope thickly covered fields of oil globules.

The experiment was concluded at the end of 19 hours 35 minutes for analyses of the contents as given below, and at this time each tube showed a thick creamy layer, perhaps slightly less in No. 4 (boiled extract), but still very obvious. All four showed, under the microscope, fields crowded with oil globules of all sizes.

*Pancreas.*

This series of tubes, when examined 1 hour after the commencement of the experiment, showed in each case a milky fluid, and the microscopic examination demonstrated abundance of oil globules.

The reaction was obviously more intense than in the case of the intestine.

After the lapse of 18 hours from the commencement of the experiment, when it was stopped to make the analyses detailed below, there was a thick creamy layer at the top of each tube which was not apparently any less in quantity in No. 4 (boiled extract) than in any of the others.

The microscope showed in all four tubes oil globules of all sizes in great number.

The eight tubes were extracted with ether, and the weights of the ethereal extracts,\* and the percentages of free oleic acid they contained, are given in the following table:—

| Contents of tubes.                     | Weight<br>of ethereal<br>extract. | Weight<br>of free oleic<br>acid. | Percentage<br>of free<br>oleic acid. |
|----------------------------------------|-----------------------------------|----------------------------------|--------------------------------------|
| Intestinal mucosa.                     | gramme.                           | gramme.                          |                                      |
| No. 1. Oleate + glycerine + dextrose.. | 0·1800                            | 0·1664                           | 92·4                                 |
| No. 2. Oleate + glycerine.....         | 0·1258                            | 0·1256                           | 99·8                                 |
| No. 3. Oleate alone.....               | 0·1582                            | 0·1466                           | 92·7                                 |
| No. 4. Oleate alone, then boiled....   | 0·1322                            | 0·1269                           | 96·0                                 |
| Pancreas.                              |                                   |                                  |                                      |
| No. 1. Oleate + glycerine + dextrose.. | 0·2668                            | 0·2580                           | 96·7                                 |
| No. 2. Oleate + glycerine.....         | 0·2568                            | 0·2312                           | 90·0                                 |
| No. 3. Oleate alone.....               | 0·2176                            | 0·2140                           | 98·3                                 |
| No. 4. Oleate alone, then boiled....   | 0·2394                            | 0·2284                           | 95·4                                 |

This experiment shows that with cell-free extracts of pancreas and intestinal mucosa the main effect obtained is a conversion of sodium oleate into free oleic acid, and that there is no appreciable formation of olein.

*Expt. 5. Control Experiment.*—It might be argued that in the preceding experiments the soap was hydrolysed by the water or saline used as a solvent, and not by any active constituent derived from the tissues extracted, and accordingly a series of controls were arranged in which the same percentage of soap was dissolved, as follows:—

- No. 1. Distilled water, 40 c.c. + sodium oleate, 0·8 gramme + glycerine, 0·4 gramme.
- No. 2. Normal saline (0·75 per cent.), 40 c.c. + sodium oleate, 0·8 gramme + glycerine, 0·4 gramme.
- No. 3. Solution of normal sodium carbonate (0·2 per cent.), 40 c.c. + saturation with carbon dioxide + glycerine, 0·4 gramme.
- No. 4. Oxalated pig's plasma, 40 c.c. + sodium oleate, 0·8 gramme + glycerine, 0·4 gramme.

\* The weighings throughout these experiments have been taken to  $\frac{1}{10}$  milligramme. The figures represent fractions of a gramme.

The four solutions were placed in the incubator at 36° C., and examined as soon as they had attained the temperature of the incubator.

No. 1 was completely dissolved to a clear solution; Nos. 2 and 3 were opalescent and contained a good deal of undissolved oleate; No. 4 was clear but contained still a small amount of undissolved oleate.

Examined again, 4 hours later, the appearances presented by the four solutions were much the same as at the previous examination, while microscopic examination showed no trace of fat globules in any of the four solutions, but merely fine amorphous granules.

An examination made 46 hours after the commencement of the experiment, during the whole of which interval the solutions had been maintained at a temperature of 36° C., showed complete clear solution in Nos. 1 and 4 without a trace of cloudiness or precipitate, and giving a clear field under the microscope. Nos. 2 and 3 were opalescent and contained sediment, but there was no layer of oil and no globules visible under the microscope.

These controls demonstrate therefore that the formation of free oleic acid found in the previous experiments was due to some hydrolytic agent present in the tissue extracts.

### *Series B.*

In the experiments of Series A, extracts free from cells were employed throughout, and as the results were different from those of previous observers who had employed the cells of the tissues, attention was now turned to similar experiments in the presence of the cells.

To make the experiments comparable with those of previous workers, the solutions, after digestion with the soap and glycerine in presence of the fresh cells, were evaporated down to dryness before extraction with ether for the determination of the nature of the fatty constituents.

By the use of this method the quantity of total ethereal extract is largely increased; but the control experiments, as well as the experiments recorded in Series C (*vide infra*), showed that the increase here obtained is due to dissolved soap and not to neutral fat.

*Expt. 1.*—The intestinal mucosa of a cat was prepared as already described, and two quantities of 6 grammes each were weighed out.

Portion No. 1 had 30 c.c. of normal saline, 0.6 gramme of sodium oleate, and 0.3 gramme of glycerine added; and portion No. 2, which was used as a control, had 30 c.c. of normal saline only added.

The two flasks containing the mixtures were placed in the incubator at 36° C. for a period of 43 hours, and were then taken out and the contents evaporated to dryness in porcelain basins on a steam bath.

When both were dry, 0.6 gramme of sodium oleate was added to No. 2, and then in each case four extractions were immediately commenced with ether. The united ethereal extracts in each case were evaporated to dryness, and the residues weighed.

Each residue was then dissolved in hot alcohol, and the amount of free fatty acid determined by titration with  $\frac{1}{10}$  N caustic soda, using phenol-phthalein as indicator.



The results are given in the following table:—

|                      | Weight<br>of ethereal<br>extract. | Weight<br>of free oleic<br>acid. | Difference.       | Percentage<br>of free<br>oleic acid. |
|----------------------|-----------------------------------|----------------------------------|-------------------|--------------------------------------|
| No. 1.....           | gramme.<br>0·6290                 | gramme.<br>0·4399                | gramme.<br>0·1891 | 69·9                                 |
| No. 2 (control)..... | 0·3708                            | 0·2510                           | 0·1198            | 67·7                                 |

The free oleic acid obtained in No. 2 is derived from the neutral fat off the intestinal mucosa and not from the sodium oleate (compare Experiment 1, Series C). The difference between free oleic acid in No. 1 and No. 2 is due to hydrolysis of the sodium oleate in No. 1, and it is evident from the differences in column 3 that there is no appreciable synthesis of neutral fat. In fact, the difference lies in the opposite direction in Experiment 2 of this series (*vide infra*), proving that the 0·0693 gramme here apparently formed (0·1891—0·1198 gramme) lies within the limit of experimental error.

*Expt. 2.*—The abdominal lymphatics of the animal used in Experiment 1 were finely divided, and treated in similar fashion to the intestinal mucosa used in that experiment.

Portion No. 1 weighed 1·82 grammes, and to this were added 18 c.c. of normal saline, 0·36 gramme of sodium oleate, and 0·15 gramme of glycerine.

Portion No. 2 weighed 1·63 grammes, and to this were added 16 c.c. of normal saline only as a control. The two mixtures were digested at 36° C. for an interval of 115 hours, both were then evaporated to dryness, and 0·32 gramme of sodium oleate was added to No. 2. Each was then extracted four times with ether, the united ethereal extracts in each case were evaporated to dryness, and the weights of total ethereal extract and amounts of free oleic acid were determined.

The results were for ease of comparison calculated to 2 grammes of tissue, and are given in the following table:—

|            | Weight<br>of ethereal<br>extract. | Weight<br>of free oleic<br>acid. | Difference.       | Percentage<br>of free<br>oleic acid. |
|------------|-----------------------------------|----------------------------------|-------------------|--------------------------------------|
| No. 1..... | gramme.<br>0·4024                 | gramme.<br>0·2751                | gramme.<br>0·1273 | 68·2*                                |
| No. 2..... | 0·3782                            | 0·1825                           | 0·1957            | 48·2                                 |

Here the difference between total extract and free oleic acid is greater in the case of the control, showing that there is no synthesis of neutral fat.

#### *Series C.*

In this series of experiments, in addition to determining the amount of free oleic acid in the ethereal extract, the amount of neutral fat was determined.

\* The lower percentage of oleic acid obtained in this and in the preceding experiment is due to the dry method of extraction, in which more soap is dissolved out than in the wet extraction employed in Series A; the difference is not due to neutral fat, but to soap, as is conclusively shown by the experiments in Series C.

also determined by Köttstorfer's saponification method (*vide supra*), and this amount was always found so low as to lie well within the limits of experimental error.\*

To save repetition it may be stated that in each experiment of the series the extract, which in some cases was cell-free and in others contained the fresh tissue cells, was divided into four portions. Portion No. 1 had 2 per cent. of sodium oleate and 1 per cent. of glycerine added; No. 2 had 2 per cent. of sodium oleate alone; No. 3 had 2 per cent. of sodium oleate added after previous boiling; and No. 4 had nothing added, and was not boiled.

A comparison of the four sets of results after digestion will accordingly show the effects, if any, of presence of glycerine, as between No. 1 and No. 2; the effect of boiling upon the production of free oleic acid, as between Nos. 2 and 3; while No. 4 gives the amount of fatty extractives and action of digestion thereon in the tissues or extracts themselves.

The four portions were subjected to digestion for a stated period, which varied in the different experiments, and were next evaporated to dryness on a steam bath, after which each dry residue was treated in the following manner:—

Four extractions were made with ether, and the amount of residue on evaporation of the united ethereal extracts gave the total ethereal extractive.

The ethereal residue was dissolved in hot alcohol and titrated with decinormal sodic hydrate, using phenol-phthaleïn as indicator, titrating rapidly and taking the first appearance of a pink tinge as the end of the reaction, so as to avoid saponification of any trace of neutral fat which might be present. This gave a figure for the calculation of the amount of free oleic acid present.

After neutralisation, the alcoholic solution had a measured amount of a standardised approximately  $\frac{1}{2}$ N solution of alcoholic potash added, and was boiled in a flask fitted with a reflux tube for 20 minutes to half an hour. The solution was then titrated back to neutrality with standard  $\frac{1}{2}$ N hydrochloric acid, and the difference gave the amount of caustic potash used in saponifying and hence a figure for the determination of the amount of neutral olein present.

*Expt. 1.*—Intestinal mucosa cells (pig) in distilled water; period of digestion, 17 hours. In each portion were placed 10 grammes of intestinal mucosa and 30 c.c. of distilled water. No. 1 had added 0.8 gramme of sodium oleate and

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\* The figures given in the various experiments are intended merely to illustrate this point and not to form determinations of small actual amounts of neutral fat, the amount of alkali apparently required in saponification never exceeding 0.25 c.c. of standard alkali. The small amount used is also the only reason for the coincidences in value in the tables.

0·4 gramme of glycerine; No. 2, 0·8 gramme of sodium oleate only; No. 3, 0·8 gramme of sodium oleate after previous boiling; No. 4 had nothing added and was not boiled previous to digestion.

The results were as follows:—

|            | Total<br>etheral<br>residue. | Free<br>oleic acid. | Olein.  | Soap, &c. |
|------------|------------------------------|---------------------|---------|-----------|
|            | gramme.                      | gramme.             | gramme. | gramme.   |
| No. 1..... | 0·8084                       | 0·1942              | 0·0294  | 0·5798    |
| No. 2..... | 0·6168                       | 0·1885              | 0·0368  | 0·3915    |
| No. 3..... | 0·5772                       | 0·1294              | 0·0368  | 0·4110    |
| No. 4..... | 0·0526                       | 0·0309              | 0·0211  | 0·0016    |

It is here obvious, from inspection of the third column, that the amount of olein formed, as shown by the difference between No. 4, in the olein column, and the other three, is negligible and lies well within the limit of experimental error. Column No. 4 shows that the difference between total ethereal extract and free oleic acid is due to dissolved soap.

#### ADDENDA TO THIS EXPERIMENT.

##### *a. Controls with Distilled Water.*

An experiment was next instituted to control the above and succeeding experiments of this series, by taking solutions in distilled water (*a*) of sodium oleate and glycerine, and (*b*) of sodium oleate alone, in identical strengths with those used above. The same amounts of solution, period of digestion, and modes of extracting and titrating were employed.

The following results were obtained:—

|                             | Total<br>etheral<br>extract. | Free<br>oleic acid. | Olein.  | Soap.   |
|-----------------------------|------------------------------|---------------------|---------|---------|
|                             | gramme.                      | gramme.             | gramme. | gramme. |
| No. 1 (oleate + glycerine), | 0·6152                       | 0·0704              | 0·0147  | 0·5301  |
| No. 2 (oleate alone)....    | 0·5746                       | 0·0760              | 0·0294  | 0·4692  |

This demonstrates that the chief thing dissolved and extracted in these controls was unaltered soap, and hence that the free oleic acid found in the case of the other experiments was not due to the experimental procedures employed, and further that the small amount of olein there found being no higher than here, was due to experimental error.

*b. Action of the Intestinal Extract after Evaporation to Dryness and Extraction with Ether.*

The experiment described above having shown (*vide* No. 3) that boiling, for 5 minutes, only somewhat diminished the power of the extract to convert sodium oleate into free oleic acid, and did not destroy it completely, the residue of No. 4, weighing 0·5786 gramme, to which no soap had been added, and which had now been not only boiled but reduced to dryness on the steam bath, and then subsequently exhausted with ether so that it contained no fat, was now tested by an additional experiment as to whether it still possessed any activity upon sodium oleate.

For this purpose it was treated with 40 c.c. of distilled water, and 0·8 gramme of sodium oleate was added to the mixture, which was then digested at 36° C. for a period of 17 hours; afterwards extraction was made with ether as before, and determinations made of total ethereal extract, free oleic acid, and olein with the following results:—

| Total ethereal extract. | Oleic acid.       | Olein.            | Soap.             |
|-------------------------|-------------------|-------------------|-------------------|
| gramme.<br>0·5352       | gramme.<br>0·2769 | gramme.<br>0·0147 | gramme.<br>0·2446 |

A comparison of the columns for oleic acid and soap with those obtained in the preceding control with distilled water only is sufficient to demonstrate that the activity of the extract, although somewhat impaired, is by no means destroyed by evaporation down to dryness at 160° C.

*Expt. 2.—Digestion with intestinal mucosa cells (pig) in distilled water for a shorter period (interval 2½ hours).*

The quantities and experimental procedures were as in Experiment 1, but the time of digestion was here reduced from 17 hours to 2½ hours, and the results were as follows:—

|           | Total ethereal extract. | Oleic acid. | Olein.  | Soap.   |
|-----------|-------------------------|-------------|---------|---------|
|           | gramme.                 | gramme.     | gramme. | gramme. |
| 0. 1..... | 0·5588                  | 0·1664      | 0·0073  | 0·3851  |
| 0. 2..... | 0·3956                  | 0·1382      | 0·0147  | 0·2427  |
| 0. 3..... | 0·5834                  | 0·1382      | 0·0060  | 0·4452  |
| 0. 4..... | 0·0432                  | 0·0169      | 0·0294  | 0·0600* |

The quantities of oleic acid here formed are almost as large as in the previous experiment, lasting 17 hours, showing that equilibrium had practically been attained in 2½ hours.

\* In No. 4 the added oleic acid and olein slightly exceed the total ethereal extract, this is of course due to experimental error.

*Expt. 3.*—Intestinal mucosa cells (pig) in 0·75 per cent. saline, quantities and procedures as before, interval 2½ hours :—

|            | Total<br>etheral<br>extract. | Oleic acid. | Olein.  | Soap.   |
|------------|------------------------------|-------------|---------|---------|
|            | gramme.                      | gramme.     | gramme. | gramme. |
| No. 1..... | 0·4620                       | 0·1269      | 0·0147  | 0·3204  |
| No. 2..... | 0·3224                       | 0·1269      | 0·0073  | 0·1882  |
| No. 3..... | 0·2706                       | 0·0733      | 0·0147  | 0·1826  |
| No. 4..... | 0·0224                       | 0·0·97      | 0·0147  | 0·0000* |

*Expt. 4.*—Clear intestinal mucosa extract (pig) in distilled water, 1 of gland to 5 of water; period of extraction = 44 hours; period of digestion = 2½ hours. Quantities taken and procedures as before :—

|            | Total<br>etheral<br>extract. | Oleic acid. | Olein.  | Soap.   |
|------------|------------------------------|-------------|---------|---------|
|            | gramme.                      | gramme.     | gramme. | gramme. |
| No. 1..... | 0·3552                       | 0·2171      | 0·0147  | 0·1234  |
| No. 2..... | 0·3338                       | 0·2284      | 0·0220  | 0·0834  |
| No. 3..... | 0·3292                       | 0·1916      | 0·0147  | 0·1199  |
| No. 4..... | 0·0302                       | 0·0197      | 0·0220  | 0·0000  |

*Expt. 5.*—Clear intestinal mucosa extract (pig) in 0·75 per cent. saline, 1 of gland to 5 of saline; period of extraction = 44 hours; period of digestion = 2½ hours :—

|            | Total<br>etheral<br>extract. | Oleic acid. | Olein.  | Soap.   |
|------------|------------------------------|-------------|---------|---------|
|            | gramme.                      | gramme.     | gramme. | gramme. |
| No. 1..... | 0·3252                       | 0·1946      | 0·0073  | 0·1233  |
| No. 2..... | 0·3586                       | 0·2171      | 0·0073  | 0·1342  |
| No. 3..... | 0·4774                       | 0·2143      | 0·0147  | 0·2484  |
| No. 4..... | 0·0152                       | 0·0085      | 0·0147  | 0·0000  |

*Expt. 6.*—Pancreatic cells (pig) in 0·75 per cent. saline, 1 of gland to 7 of saline; period of digestion = 15 hours. Quantities and procedures as before :—

|            | Total<br>etheral<br>extract. | Oleic acid. | Olein.  | Soap.   |
|------------|------------------------------|-------------|---------|---------|
|            | gramme.                      | gramme.     | gramme. | gramme. |
| No. 1..... | 0·9330                       | 0·6796      | 0·1323  | 0·1211  |
| No. 2..... | 0·9922                       | 0·7363      | 0·1617  | 0·0945  |
| No. 3..... | 0·7518                       | 0·2763      | 0·1941  | 0·2314  |
| No. 4..... | 0·3036                       | 0·2058      | 0·0955  | 0·0023  |

\* See ante.

The olein found in this experiment arises from the fat present in the pig's pancreas (compare Experiment 7). The amount in No. 4 is less indeed than in Nos. 1, 2, and 3, but this is most probably due to the protective action of the soap present which is attacked by the active substance of the gland.

*Expt. 7.*—Clear pancreatic extract (pig) in 0.75 per cent. saline, 1 of gland to 7 of saline; period of extraction = 23 hours; period of digestion = 16 hours:—

|            | Total<br>etheral<br>extract. | Oleic acid. | Olein.  | Soap.   |
|------------|------------------------------|-------------|---------|---------|
|            | gramme.                      | gramme.     | gramme. | gramme. |
| No. 1..... | 0.5344                       | 0.4766      | 0.0073  | 0.0505  |
| No. 2..... | 0.4582                       | 0.4484      | 0.0073  | 0.0025  |
| No. 3..... | 0.5212                       | 0.4596      | 0.0073  | 0.0543  |
| No. 4..... | 0.0396                       | 0.0282      | 0.0147  | 0.0000  |

*Expt. 8.*—Abdominal lymphatic cells (pig) in 0.75 per cent. saline, 1 of gland to 7 of saline; period of digestion = 15 hours:—

|            | Total<br>etheral<br>extract. | Oleic acid. | Olein.  | Soap.   |
|------------|------------------------------|-------------|---------|---------|
|            | gramme.                      | gramme.     | gramme. | gramme. |
| No. 1..... | 0.6738                       | 0.2961      | 0.0073  | 0.3704  |
| No. 2..... | 0.5766                       | 0.2933      | 0.0058  | 0.2775  |
| No. 3..... | 0.5062                       | 0.1720      | 0.0080  | 0.3262  |
| No. 4..... | 0.0754                       | 0.0296      | 0.0044  | 0.0114  |

*Expt. 9.*—Clear extract of abdominal lymphatic gland cells (pig) in 0.75 per cent. saline, 1 of gland to 7 of saline; period of extraction = 23 hours; period of digestion = 16 hours:—

|            | Total<br>etheral<br>extract. | Oleic acid. | Olein.  | Soap.   |
|------------|------------------------------|-------------|---------|---------|
|            | gramme.                      | gramme.     | gramme. | gramme. |
| No. 1..... | 0.5382                       | 0.4174      | 0.0294  | 0.0914  |
| No. 2..... | 0.4472                       | 0.3722      | 0.0147  | 0.0603  |
| No. 3..... | 0.4612                       | 0.3638      | 0.0294  | 0.0680  |
| No. 4..... | 0.0266                       | 0.0282      | 0.0147  | 0.0000  |

*Summary of Results and Conclusions.*

1. Analyses of the lymph contained in the mesenteric lymphatic vessels during fat absorption demonstrate that at this stage of absorption practically all of the fatty constituents formed in the intestine during digestion have been re-synthesized into neutral fat.

This points to synthetic processes occurring in the cells present in the intestinal wall, and to the further conclusion that the cells of the mesenteric lymphatic glands are not normally concerned in the process of synthesis of the absorbed fatty constituents.

2. Analyses of the fatty constituents of the intestinal mucosa during fat absorption show a preponderance of neutral fat, but at the same time a considerable percentage of free fatty acid, showing that the synthesis is in progress, and has not obtained that completion found in the mesenteric lymphatic vessels.

3. No synthesis of neutral fat has been obtained from the normal cleavage constituents of fat (viz. soap and glycerine), by the action *in vitro* either of cells of the pancreas, intestinal mucosa or lymphatic glands, or of cell-free extracts of those tissues.

This observation taken in conjunction with the results above mentioned proves that the living cell *in situ*, supplied with energy by the circulating blood, is capable of inducing a synthesis, which is not brought about by the detached cell or substances extracted from it.

A large number of similar synthetic actions of gland cells have been observed throughout the body, and this points to an important function of the cell as an energy transformer in such reactions as are endothermic in character, and require a supply of external energy. The action of a chemical catalyser or enzyme is simpler in character. The same enzyme cannot in any known case induce two different types of chemical transformation, one running exo-thermically and the other endo-thermically, and in so doing use up the energy re-acquired from the exo-thermic reaction. This is the essential difference between the chemical activity of the living cell when supplied by energy, and that of the enzyme, which in each specific instance is confined to a reaction of a single type.

An example is given by the transformation of carbohydrate into fat; here part of the carbohydrate is oxidised by the cell, and the energy obtained in this process is utilised for the conversion of another portion of the carbohydrate into fat with the taking up of energy. In most cases the reactions brought about, or increased in velocity, by enzymes are exo thermic in character, giving rise to substances with less chemical energy than those from which they are formed, and in the few recorded cases of syntheses by enzymes, the products formed in the syntheses possess no measurably greater amount of energy than those from which they are formed.

The living cell from this point of view must be regarded as an energy transformer of much more complex type than the chemical catalyser or enzyme, and capable of producing, as shown by the present experiments, synthetic changes which do not occur as the result of the action of its chemical constituents when the complex structure of the cell is broken down, and its function as a whole abolished.

4. Extracts of pancreas, intestinal mucous membrane, and mesenteric lymphatic glands, possess the power of setting free oleic acid from solutions of sodium oleate.

The alkali split off from the sodium oleate becomes stably combined with some substance in the extracts and does not recombine with the oleic acid on evaporating down the solutions.

The power of setting free the oleic acid is diminished, but not destroyed, by boiling, nor even by evaporating the extracts to dryness.

The change occurs in faintly alkaline solution and is completed without the reaction becoming acid.

No similar change is obtained under the conditions of concentration of the experiment with water or saline solution, and hence the reaction is due to some substance in the extracts.

Such a change may possibly in the cell be the initial change which the soap undergoes in the synthesis into neutral fat.

The change obviously will act as a protection to the cells of the body against invasion by poisonous soaps in the circulation, and here serves a similar function to that seen in the conversion of the albumoses into coagulable proteids by the intestinal cells.

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"Observations on the Physiology of the Cerebral Cortex of the Anthropoid Apes." By A. S. F. GRÜNBAUM, M.D., F.R.C.P., and C. S. SHERRINGTON, M.A., M.D., F.R.S. Received May 25. —Read June 11, 1903.

(From the Physiological Laboratory, University of Liverpool.)

Since presenting our former note on this subject, we have obtained some further observations, though the number is still less than we should wish, owing to the rarity and expense of the material. Our further observations have been upon five chimpanzees of the commoner variety, and upon one more orang.

The statements given in our former communication have been confirmed in all respects by our observations obtained since then. We can, further, now make the following statements in addition :—

The whole of the surface of the "island of Reil" has proved "inexcitable" under faradisation with currents even considerably more intense than those sufficing to excite muscular movements when applied to the pre-central convolution. This is noteworthy because the large extent of the insula is a character distinguishing the brain of the anthropoid apes from that of the lower apes, and bringing it nearer toward the human type.

Faradisation of the cortex of the inferior frontal convolution in either hemisphere has failed in our hands so far to elicit movements of any satisfactory degree of regularity or constancy; and this even under use of currents much stronger than those which suffice when applied to the "motor" cortex proper. The movements for which, in particular, careful search was made, were those connected with vocalisation. From the posterior region of the convolution, at scattered points, and without constancy even at them, strong faradisation occasionally seemed to induce movements in the larynx, distinguishable from the rhythmic of respiratory origin. Judging from such evidence as we altogether obtained, we conclude that either (1) no Broca "speech centre," at all distantly foreshadowing the human, exists in these anthropoid brains, or (2) that direct faradisation of the Broca speech cortex is inefficient itself to evoke vocalisation. These two inferences, are, of course, not mutually exclusive, and both the suppositions may be correct.

Repeated observations on excitation of the cortex of the pre-central convolution confirm an opinion we had formed at the time of our former communication, and indicated in the diagram then furnished, but not verbally expressed. This is to the effect that the anterior limit of the "motor" field is not of sharp, abrupt character, but fades off forward somewhat gradually. This edge extends further forward under "*Bahnung*." Under general conditions producing lowered

excitability of the cortex it retires backward in the direction of the central fissure.

In a similar manner the boundary of the area for any particular movement, may by "*Bahnung*" be extended beyond its average limit. The special form of movement provoked from a given spot of cortex is thus influenced by the particular forms of movement excited from neighbouring points just antecedently.

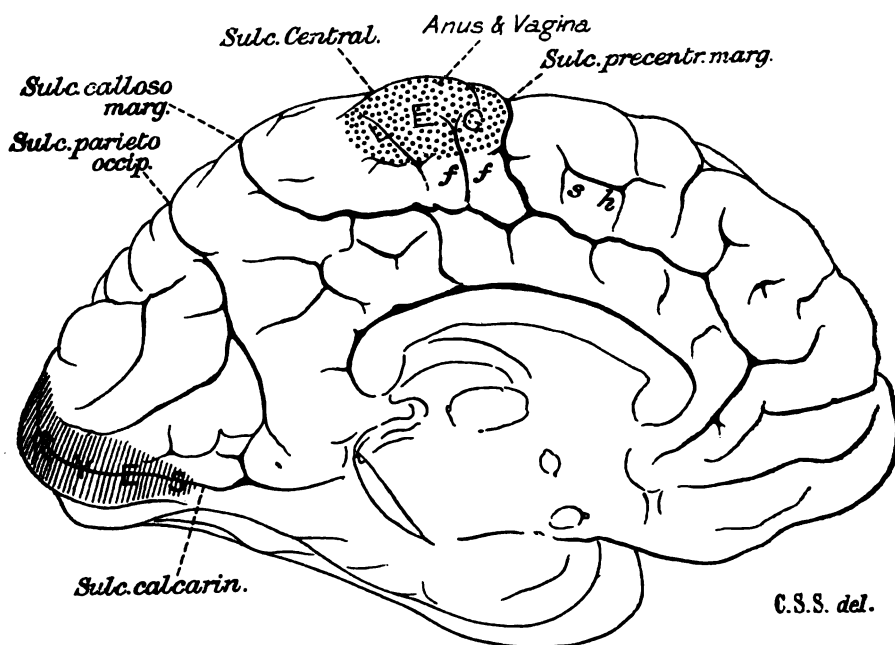
Among movements elicited from the cortex of the "facial" region, we have in two instances seen protrusion of the tongue, succeeded by forcible closure of the jaws following rapidly before retraction had withdrawn the tongue behind the arcades of the teeth; so that in these instances the tongue was caught by the closure of the teeth. This sequence of movements presents interest, as evidencing that a sequence of movement evoked by excitation of the cortex may exhibit in some respects faulty co-ordination. The movement, is also of interest as a result of direct cortical excitation which harmonises with the biting of the tongue in epileptic seizures.

Ablation of the facial area of the "motor" region was performed in one individual. A crossed hemiparesis ensued in the lips, cheek, tongue, nasal fold, and lower eyelid (very slight), but not in the upper lid, eyebrow, or frontal region.

As to the recovery of movement that occurs in a limb rendered parietic by ablation of its cortical area in the "motor" region, we find the following points: If all the area, which when faradised evokes movements of fingers, thumb, and wrist primarily, and not as a later sequel to movements starting elsewhere, be excised, the parietic condition of the hand which ensues is severe, but rapidly diminishes. In a few weeks the hand is again very fairly and freely used. If, then, the whole of the corresponding area in the opposite hemisphere is removed, a similar paresis similarly ensues in the other hand, and runs a similar course; but this second lesion does not produce, so far as we have been able to discover, the slightest recrudescence of the paresis already recovered from in the first hand. On the contrary, the first hand is almost at once employed more freely and successfully than prior to the second operation, presumably because of greater inducement to use it during the disability existing in the second hand. If, then, later, after the second hand has regained its use, the remaining part of the arm area first operated upon be ablated, this causes no obvious recrudescence of paresis either in the first hand or in the second hand. It causes severe paresis at shoulder, and to some extent at elbow, on the side crossed to the lesion, but this, again, is in great part of temporary character, and is largely recovered from. In accord with the absence of recrudescence of the hand paresis on ablating in the third operation the remaining intact part of the arm area, we found that faradisation of that part (elbow and shoulder) provoked, as

usual, movements of elbow and shoulder, but not of hand itself, or only of hand late in a general arm movement, and that very rarely. In short, neither the ablation or the excitation methods gave any evidence that the remaining part of the arm area had taken on the functions of the ablated hand area. The recovery of hand movement seems, therefore, not due to either the adjacent cortex of the same hemisphere, or to the corresponding hand area of the cortex of the opposite hemisphere, taking on the functions of the ablated cortical hand area.

Faradisation of the cortex of the post-central convolution, though



not like the pre-central itself eliciting movement, when employed at certain places facilitates the elicitation of movement by faradisation at certain points at about the same horizontal level in the pre-central convolution. In other words, from certain parts of the post-central convolution, a facilitating influence (*Bahnung*) can be exerted upon somewhat adjacent parts of the pre-central convolution.

Removal of the adjacent levels of the pre-central convolution does not render the post-central convolution "excitable;" that is to say, destruction of the pre-central convolution does not make it the more possible to obtain movements under faradisation from the post-central convolution.

\* The motor cortex of the infant chimpanzee, a few weeks old, is

readily excitable by faradisation. Its reactions do not appear to differ obviously in this respect from those obtainable from the adult. The movements it yields are not choreiform in character.

The spinal degeneration ensuing upon ablation of the arm area of the motor cortex of the chimpanzee, although it sometimes reveals a large uncrossed ventral pyramidal tract (direct Py. Tr.), does not do so in every case. Even after bilateral arm area lesions, the ventral pyramidal degeneration in the spinal cord may be very slight. The anthropoid cord resembles the human, therefore, not only in the possession of this tract, but in exhibiting in regard to it a remarkable degree of individual variation of development as Flechsig showed to be the case in man.

The expenses of this research have been in part defrayed by a grant kindly allowed by the Scientific Grants Committee of the British Medical Association.

#### DESCRIPTION OF FIGURE.

Brain of a chimpanzee (*Troglodytes niger*). Left hemisphere; mesial surface. The extent of the "motor" area on the free surface of the hemisphere is indicated by the black stippling. On the stippled area "LEG," indicates that movements of the lower limb are directly represented in all the regions of the "motor" area visible from this aspect. Such mutual overlapping of the minuter sub-divisions exists in this area that the diagram does not attempt to exhibit them. The pointing line from "Anus, etc.," indicates broadly the position of the area whence perineal movements are primarily elicitable.

*Sulc. Central.* = central fissure. *Sulc. calcarin.* = calcarine fissure. *Sulc. parieto occip.* = parieto-occipital fissure. *Sulc. calloso marg.* = calloso-marginal fissure. *Sulc. precentr. marg.* = pre-central marginal fissure.

The single italic letters mark spots whence, occasionally and irregularly, movements of the foot and leg (*ff*), of the shoulder and chest (*s*), and of the thumb and fingers (*h*) have been evoked by strong faradisation. Similarly the shaded area marked "EYES" indicates a field of free surface of cortex which under faradisation yields conjugate movements of the eyeballs. The conditions of obtainment of these reactions separates them from those characterising the "motor" area.

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"Separation of Solids in the Surface-layers of Solutions and 'Suspensions' (Observations on Surface-membranes, Bubbles, Emulsions, and Mechanical Coagulation).—Preliminary Account." By W. RAMSDEN, M.A., M.D., Oxon., Fellow of Pembroke College, Oxford. Communicated by Professor F. GOTCH, F.R.S. Received June 8,—Read June 18, 1903 —

In a paper published in Du Bois Reymond's 'Archiv für Anat. und Physiologie' in 1894,\* I showed that mere agitation of various proteid solutions brought about a separation of some of their contained proteid in the form of fibrous or membrano-fibrous solids, and that it was possible in this way to coagulate and remove the whole of the proteid from solutions of egg-albumin. It was proved also that these de-solutions and coagulations of proteid were not due to the action of enzyme, heat, or surface evaporation, and were not appreciably affected by the nature of the gas in contact with the liquid or of the vessel in which the agitation was effected.

A prolonged series of further experiments, undertaken with a view of ascertaining the precise cause of this phenomenon, has led me to the discovery of an important, but hitherto unnoticed physical fact:—namely, that, quite apart from evaporation, solid or highly viscous coatings are spontaneously, and more or less rapidly formed on the free surfaces of all proteid solutions.

By purely mechanical means these free-surface coatings can be heaped up to form visible solid masses of proteid, which in some cases is not only "de-solved," but at the same time coagulated and rendered permanently insoluble in the mother-liquid.

By extending the range of my experiments, I have been led to the further conclusion that similar coatings of solid or highly viscous matter occur on the free surfaces of a large number of non-proteid colloidal solutions, of fine and coarse "suspensions," and of a few apparently crystalloid solutions, and that they are formed also at the interfaces of every pair of liquids which, without being of high viscosity, are capable of forming persistent emulsions.

The explanation of these spontaneous de-solutions of previously dissolved matter at the free surfaces must be sought in the observations which I have found to hold good in all cases hitherto examined, that the matter which accumulates possesses the property of lowering the surface-tension, and, therefore, the "surface energy," of the free surface of water.

On dynamical grounds, the most stable arrangement of any solution

\* "Physiologische Abtheilung" pp. 517—534.

taking surface-tension considerations only into account, must be one accompanied by minimal "surface energy." A dissolved substance, if it increases the potential energy of a surface, will tend to leave that surface, or if it diminishes it, to accumulate at that surface. This principle has been recognised as holding good in crystalloid solutions\* but has not hitherto been shown to apply to colloid solutions and coarse "suspensions."

The same considerations may be applied in explanation of the accumulations observed at the interfaces of liquids forming persistent emulsions.

The formation of surface pellicles, the separation of various solids by mechanical treatment adapted to produce heaping up of surface-films, the power of forming moderately persistent bubbles possessed by various limpid solutions, and the power of forming persistent emulsions possessed by various immiscible liquids, are all explained (in the numerous cases where there is no evidence of chemical change) as due to diminution of the surface-energy brought about by accumulation of certain dissolved or suspended matters at the surfaces concerned, and to the physical properties of the accumulated material.

It is remarkable that the very common occurrence of these free-surface accumulations has hitherto escaped general notice. Doubtless this is due to the extreme delicacy and fragility of the solid coating, and to its generally rapid re-solution when by contraction of the surface it is heaped up in local excess, or when by the substitution of some other surface, the reason for such accumulation has been removed. For the production of *visible* masses of solid, or of deformed angular bubbles, it is in fact necessary that the surface-solid shall either be rendered insoluble by the mechanical treatment to which it is subjected, or shall be heaped up more rapidly than it is re-dissolved.

Full details of the methods employed, the control experiments made, and the results obtained, together with references to the work of others in the same field, I hope to publish shortly. Meanwhile a brief summary of the main points will be found in the following observations:—

1. The presence of a free (*i.e.*, gas) surface is essential for the production of the de-solutions and coagulations described in my previous paper.

2. By simple and gentle mechanical means adapted to produce heaping up of the surface-films, large masses of solid ("mechanical surface aggregates") can be separated out from all proteid solutions and from a large number of colloid solutions and suspensions. (*Vide* table at end of paper.) In the three cases where the dilution-limit has been ascertained, solid "mechanical surface aggregates" have been

\* *Vide* J. J. Thomson, "Application of Dynamics to Physics and Chemistry," p. 251.

obtained from liquids containing as little as one part of dissolved or suspended solid in 1,000,000 parts of water.

3. The separated solids differ greatly from one another in the rapidity and completeness of their re-solubility in the mother liquid, and they are sometimes insoluble and "coagulated."

4. They may have a delicate membranous, membrano-fibrous, or fibrous structure, simulating that of various biological tissues, or they may consist of particles lying loosely side by side (*e.g.*, sulphur).

5. The film of the free surface of all proteid solutions, and many of the various solutions or suspensions which yield solid "mechanical surface aggregates," exhibits a specially high viscosity not met with in the bulk of the solution. This "special superficial viscosity" develops at very different rates in different solutions, and attains very different degrees of maximal intensity. In some solutions (*e.g.*, egg-albumin, saponin) it develops with great rapidity; in others (*e.g.*, serum-albumin, methyl-orange, ferric acetate, mastic, etc.) several minutes or even hours may be necessary for any considerable development. Evaporation hastens its development, but is not essential. Slight convection currents have a powerful accelerating influence, but are essential only when the suspended solid is indiffusible. The nature of the gas in contact with the "solution" is a matter of indifference, provided it be chemically inactive.

6. In most cases the "special superficial viscosity" is accompanied by a special superficial resistance to "shear." This is often so intense that a magnetised needle floating on the solution is capable of rotating the vessel containing the solution, if this be floated on water or suspended by a fine thread and the needle be exposed to the attraction of a magnet.

7. The presence on a liquid of a thin coating of matter (even of liquid) which diminishes the "surface energy" would account for some "special superficial viscosity" (Marangoni), but would not account for superficial resistance to "shear," unless the coating of matter were solid or highly viscous and also coherent.

8. Bubbles of solutions of egg-albumin, caseinogen and saponin exhibit remarkable phenomena, which show that the bubble-film as a whole is very imperfectly elastic and is covered with solid membranes. Egg-albumin bubbles are deformed on collapse by the formation of persistent folds of solid proteid in the bubble-film. Bubbles of pure saponin solution, containing 0.01 per cent. or more of saponin, fall on collapse into innumerable shimmering folds containing isolated curved rods of solid saponin, although water is capable of dissolving at least 2500 times this amount.

The collapsing bubble assumes extraordinary shapes, with sharp angles (as observed by Plateau), and when a hanging bubble is broken, ragged curtain of bubble-film, which instantly becomes dull and

opalescent, hangs for some 5 or 10 seconds from the edge of the supporting tube.

9. The presence of such solid membranes on a bubble must contribute greatly to its persistence. Further, the mere presence of solid particles on the surfaces of a bubble has, in many cases, been found to add greatly to its persistence, even when, judging by the absence of a special resistance to shear in the film of a free surface of the solution, such particles are not appreciably coherent, but lie loosely side by side (*e.g.*, in suspensions of sulphur, picric acid, quinine bisulphate, salicylic acid).

In the cases quoted, a bubble of air can be seen to pick up the particles in suspension as it passes through the liquid, and to retain them obstinately when it reaches the surface and comes to rest, so that the bubble becomes thickly coated with solid particles, although the liquid contained only a small quantity of suspended solid, and this solid is specifically heavier than the solution.

10. Every solution capable of forming moderately persistent bubbles which has hitherto been examined has yielded solid or highly viscous mechanical surface aggregates. This very remarkable fact indicates that the power of forming such bubbles is due to the presence of matter which has accumulated at the free surfaces in a solid or highly viscous condition. The cohesion of the matter, so as to form an appreciably coherent membrane, is apparently not essential, but it occurs in most cases where the bubble is very persistent.

Plateau recognised this association of the power of forming persistent bubbles with a special superficial viscosity and a diminished surface-tension, but did not connect these phenomena with the formation of a coating of matter derived from the solution and specially concentrated at a free surface.\*

On theoretical grounds the presence of a thin film of liquid, even of low viscosity, on the free surfaces, should also be capable of increasing the persistence of a bubble if the liquid be such as diminishes the surface energy of the mother solution, but increased persistence brought about in this way appears to be very slight compared with that occurring when the coating consists of solid or highly viscous particles.

11. The effects which the presence of solid particles in the surface layer exercises upon the persistence, size and other properties of bubbles, depend on many factors. Many solutions in which surface accumulation of solid undoubtedly takes place have been found incapable of forming large or persistent bubbles. The size of the particles, their surface-tension relations, the rate of their accumulation, the rate of their re-solution when forced by mechanical means into local excess, and the elasticities and flexibility of any membrane

\* *I'ide* 'Statique des Liquides,' pp. 69—71.



formed, are all concerned in conferring on different bubbles the marked individuality which characterises them, and in making the formation of large or persistent bubbles possible. Solid particles, which diminish the surface energy of the free surface, may be regarded as adding in three ways to the persistence of a bubble:—

- i. By serving as *points d'appui*.\*
- ii. By actual contact, friction, or cohesion of the particles, opposing local disturbances of the film.
- iii. By opposing such deformation of the surface as tends to expose a new surface with higher surface-tension (*i.e.*, like oil on water, by the effect of the surface coating in diminishing the superficial energy).

12. It has been demonstrated that an actual solid membrane forms around the globules of several persistent emulsions, and at the contact interfaces of several pairs of liquids capable of forming persistent emulsions (*e.g.*, pure neutral olive oil and saponin solutions).

The membrane manifests itself by producing the following phenomena:—

- i. Intense viscosity peculiar to the interface, absent at the interface of pure water and the other liquid, and developing only when an emulsifying substance is added to one or other of the liquids.
- ii. Persistently deformed sharply angular and grotesque shapes of the emulsified globules.
- iii. Folds of semi-opaque membrane when the surface of separation is subjected to appropriate deformation.

Such direct optical evidence of the presence of a constraining membrane separating liquids which form persistent emulsions is exceptional or, if it occur, is usually fugitive. (*Cf.* air-bubbles.) An intense "special interface viscosity," pointing to the presence of solid or highly viscous matter, has, however, been found with every pair of liquids capable of forming persistent emulsions hitherto examined.

13. The persistence of many emulsions is therefore determined largely, among other factors, by the presence of solid or highly viscous matter at the interfaces of the two liquids. Direct measurements of the various surface tensions concerned are not available, but the close resemblance of the phenomena to those occurring at a free surface points to the view that accumulation of solid matter at the interfaces of the above emulsion-pairs occurs because the "surface-energy" is thereby diminished.

14. Numerous precipitations of colloids from their solutions by chloroform, ether, carbon bisulphide and amyl-alcohol, are attended by

\* *Cf.* Frankenheim, 'Die Lehre von der Cohäsion': Breslau, 1835.

precisely similar phenomena at the interfaces of the liquids concerned, and appear to be brought about in exactly the same way.

15. The suggestion that the observed surface accumulations must be attributed to the diminution of the "superficial energy" thereby produced is strongly supported by a series of experiments made with watery solutions containing equal quantities of two substances each of which by itself forms "mechanical surface aggregates." In such mixtures there has invariably been preferential accumulation of one substance to the more or less complete exclusion of the other from the mechanical surface aggregate obtained. Thus—

|             |                |
|-------------|----------------|
| Saponin     | > Egg-albumin. |
| Bile-salts  | > Saponin.     |
| "           | > Soap.        |
| "           | > Gamboge.     |
| "           | > Egg-albumin. |
| "           | > Sulphur.     |
| Egg-albumin | > Carmine.     |

If the dissolved substances thus mixed exert no chemical action upon each other, such preferential accumulation is not only explicable, but, taking only surface-tension considerations into account, is theoretically essential when one substance produces a greater diminution of the surface energy than the other. In actual practice, however, the phenomena are complicated by differences in diffusibility and rate of re-solution and by limitation of independent mobility of the "dissolved" particles due to their mutual cohesions and adhesions.

16. It has been found also that bubbles blown from mixed solutions of two substances, each of which by itself forms bubbles presenting recognisable and well-marked differences of character, behave precisely as if they had been blown from a solution of one of these substances only, and this is always the one which in a mechanical surface aggregate made from the mixed solution is found to have more or less completely excluded the other, *e.g.* :—

|             |                |
|-------------|----------------|
| Saponin     | > Egg-albumin. |
| Bile-salts  | > Saponin.     |
| "           | > Egg-albumin. |
| Egg-albumin | > Carmine.     |

17. The fact that the introduction of alcohol (and of other liquids of low surface-tension) into many solutions which show the above described surface phenomena frequently deprives those solutions of their superficial viscosity and of their power of forming bubbles or of yielding mechanical surface aggregates, would seem to be explicable by similar considerations, *i.e.*, as due to preferential

accumulation of alcohol to the exclusion of the suspended or dissolved solid.

18. Various hitherto obscure phenomena find their explanation the facts observed, *e.g.* :—

- i. The ready formation of a "skin" on hot milk exposed to evaporation is explained by (a) The presence of a delicate skin or pellicle on the free surface even of cold milk or of caseinogen solutions not exposed to evaporation; (b) The presence of a similar pellicle at the inter-faces between caseinogen solutions and pure neutral olive oil or butter fat.

The existence of a proteid "haptogen-membrane" around the cream-globules of milk cannot any longer be doubted, and their rôle in contributing to the ready formation of a thick skin on hot milk, as first demonstrated by Hertz and Jamison,\* finds a complete explanation. The apparently contradictory observations of Kettger,† demonstrating the possibility of obtaining very delicate skins by heating caseinogen and other solutions, although free from fat globules, appear to be due to the dehydration and thickening by evaporation of the surface pellicle present on such solutions even in the cold.

- ii. The homogeneous "Grenz-membran" described by Bütschli (an optical homogeneity of thin films referred to by Hardy) in various coagulated or dehydrated colloids, is the above-described membrane of solid colloid formed at an air or other appropriate surface.
- iii. The high pressure required to force solutions of saponin and albumin through capillary tubes when bubbles of air are present is largely due, among other factors, to the presence of solid membranes around the air-bubbles, and the increased resistance to deformation thus brought about. As Plateau showed, the resistance offered is enormously greater than that of water containing similar air bubbles. (Cf. air-embolism in the blood-capillaries of a mammal.)
- iv. The failure of proteids and other colloids in solution to pass through fine filters without considerable loss is largely due to the formation of surface membranes and mechanical coagula upon air, grease, or other suitable surfaces in the pores of the filter.

19. The following table indicates some of the substances whose aqueous solutions or suspensions have shown evidence of the accumulation of solid or highly viscous matter on their free surfaces, either by

\* *Ibid* 'Journ. of Physiol.,' London, 1901, vol. 27, p. 26.

† *Ibid* 'Amer. Journ. of Physiol.,' May, 1902.

| ons solutions or<br>sensions" of— | Solid<br>mechanical<br>surface<br>aggregates. | Intense<br>superficial<br>viscosity. | Persistent<br>bubbles. |
|-----------------------------------|-----------------------------------------------|--------------------------------------|------------------------|
| egg-white—                        |                                               |                                      |                        |
| to 1 in 100,000.....              | +                                             | +                                    | +                      |
| 00,000.....                       | +                                             | —                                    | —                      |
| 0 0,000.....                      | —                                             | —                                    | —                      |
| egg-albumin.....                  | +                                             | +                                    | +                      |
| ids.....                          | +                                             | +                                    | +                      |
| nin.....                          | +                                             | +                                    | +                      |
| .....                             | +                                             | +                                    | +                      |
| un.....                           | +                                             | +                                    | +                      |
| n.....                            | +                                             | +                                    | +                      |
| in clear solution in              |                                               |                                      |                        |
| solution.....                     | +                                             | +                                    | +                      |
| .....                             | +                                             | +                                    | +                      |
| umose.....                        | +                                             | +                                    | +                      |
| lbumose.....                      | +                                             | +                                    | +                      |
| from peptic digestions)           |                                               |                                      |                        |
| absolute alcohol.....             | +                                             | +                                    | +                      |
| aids.....                         | +                                             | +                                    | +                      |
| n from lentil seeds.....          | +                                             | +                                    | +                      |
| nitrate.....                      | +                                             | +                                    | +                      |
| te.....                           | +                                             | +                                    | +                      |
| ge.....                           | +                                             | +                                    | +                      |
| .....                             | +                                             | +                                    | +                      |
| ple.....                          | +                                             | +                                    | +                      |
| a 100 to 1 in 100,000...          | +                                             | +                                    | +                      |
| n 1,00,000..                      | +                                             | +                                    | —                      |
| n 10,000,000.....                 | —                                             | —                                    | —                      |
| .....                             | +                                             | +                                    | +                      |
| .....                             | +                                             | —                                    | +                      |
| te.....                           | +                                             | +                                    | +                      |
| ste.....                          | +                                             | +                                    | +                      |
| rrie hydrate.....                 | +                                             | +                                    | +                      |
| .....                             | +                                             | —                                    | +                      |
| lphur.....                        | +                                             | —                                    | +                      |
| dyslysin).....                    | +                                             | +                                    | +                      |
| .....                             | Viscous gum                                   | —                                    | +                      |
| .....                             | +                                             | +                                    | +                      |
| .....                             | +                                             | +                                    | +                      |
| .....                             | +                                             | +                                    | +                      |
| lage (1 per cent).....            | +                                             | —                                    | —                      |
| in 1,000.....                     | +                                             | —                                    | +                      |
| in 1,000,000.....                 | +                                             | —                                    | —                      |
| f sulphur".....                   | +                                             | —                                    | +                      |
| recoal.....                       | +                                             | —                                    | +                      |
| ulphate (so ution).....           | —                                             | —                                    | —                      |
| ulphate (excess in suspen-        |                                               |                                      |                        |
| ation.....                        | +                                             | —                                    | +                      |
| (solution).....                   | —                                             | —                                    | —                      |
| (ex. ess in suspension)....       | +                                             | —                                    | +                      |
| d (solution).....                 | —                                             | —                                    | —                      |
| d (excess in suspension)..        | +                                             | —                                    | +                      |

(1) yielding "mechanical surface aggregates;" (2) intense special superficial viscosity; or (3) forming persistent bubbles.

It will be seen that there is a very considerable parallelism in the three phenomena. Exact parallelism could not be expected, since the different physical properties of the surface accumulations must necessarily affect the phenomena in different and highly complex ways. Special superficial viscosity has only been recorded when very intense, and all minor degrees have been ignored, since the presence of dust, etc., in minute quantity may, as has been shown by Lord Rayleigh,\* produce some "superficial viscosity," and it has been practically impossible entirely to exclude such contamination. Power to form persistent bubbles has been shown by either:—

- i. The possibility of blowing 2-inch bubbles.
- ii. The formation of a froth.
- iii. The formation of small bubbles which last in closed vessels at least 30 minutes.

In all cases the substances employed have been of the greatest attainable purity, the de-soluted solids have been shown to consist of the same material as that in solution or suspension, and numerous control experiments have been made.

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\* 'Roy. Soc. Proc.,' vol. 48, pp. 127—140, 1890.

"The Xanthophyll Group of Yellow Colouring Matters." By  
C. A. SCHUNCK. Communicated by HORACE T. BROWN, F.R.S.  
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[PLATES 6 AND 7.]

*The Xanthophyll Group of Yellow Colouring Matters.*

The group under consideration comprises those colouring matters occurring in flowers, leaves, fruits, etc., which are insoluble in water but soluble in alcohol, ether, carbon-bisulphide and other organic solvents, to which collectively the name of xanthophyll has been applied. It is to these colouring matters that the characteristic yellow colour of flowers, autumnal leaves and fruits in the majority of cases is due. There are, however, present, varying in amount but generally in considerably less relative quantity, other yellow colouring matters which are soluble in water and alcohol, sparingly soluble in ether but insoluble in carbon-bisulphide; they, however, absorb the violet and ultra-violet rays without giving any absorption bands, whereas the members of the xanthophyll group transmit the ultra-violet rays and give definite absorption bands in the less refrangible region of the spectrum, whereby they may be distinguished from one another, and which is their chief characteristic feature. The present memoir is mainly a spectroscopic investigation of this group, whereby I have endeavoured to distinguish the different yellow colouring matters present in various flowers, leaves and fruits, and to show their spectroscopic relationship one to another, and which may, perhaps, be an aid to elucidate their chemical constitution, of which so little, if anything, is known so far.

The spectroscopic observations, as in a former investigation,\* were made by means of photography, an Iceland-spar prism, and quartz lenses being used, the source of light being a Welsbach incandescent gas mantle.

*Flowers.*

In all, twenty common yellow flowers were examined. The method of procedure was to obtain an alcoholic extract of the pigment contained in the petals, boiling for a short time being generally necessary to extract the whole. On cooling the hot filtered extract a fatty waxy deposit forms, in most cases, which carries down a certain quantity of the pigment with which it is deeply impregnated. The extract, filtered from this deposit, is now agitated with carbon-bisulphide which takes up the greater portion of the xanthophyll, leaving in the alcohol those colouring matters which obscure the violet

\* 'Roy. Soc. Proc.,' vol. 63, p. 391.

and ultra-violet region of the spectrum and which occur along with the xanthophyll in greater or less quantity in all flowers. In some flowers they are almost absent, while in others (as, for instance, the yellow calceolaria) they are present in a large quantity compared to the xanthophyll, and in the yellow dahlia the pigment is entirely comprised of them. These colouring matters are soluble in boiling water and alcohol, sparingly soluble in ether, but appear to be insoluble in carbon-bisulphide, and towards alkalies behave in a different manner to the xanthophylls, the alcoholic extracts becoming deeper yellow, in some cases orange, and in others (as from the yellow dahlia) brick-red, on addition of ammonia, and crimson with sodium hydrate, the original yellow colour being reproduced on neutralising with acid. On the other hand, alkalies appear to have no action upon the members of the xanthophyll group and saponifying does not appear to alter them.

It is essential for the spectroscopic investigation of the xanthophylls that the above-mentioned colouring matters be first got rid of. For if not, the bands of the former are obscured by the general absorption of the latter, and I find the separation by means of carbon-bisulphide preferable to extracting the petals first with boiling water, whereby they can also be removed, as this has a tendency to affect certain of the xanthophylls, due perhaps to the acid contained in the cell-sap.

The separation by carbon-bisulphide is effected by agitating the extract several times with equal quantities of the solvent until no more pigment is taken up; the several carbon-bisulphide portions or fractions, which vary from three to four in the case of flowers, are allowed to spontaneously evaporate and the pigment taken up again with alcohol, and then each is examined spectroscopically together with the original alcoholic extract for comparison, as well as the pigment contained in the fatty deposit and that remaining in the alcoholic extract after the carbon-bisulphide separation.

The results of the spectroscopic observations of the various flowers experimented with, show the presence of three yellow colouring matters, each giving, like chrysophyll, the crystalline substance obtained from alcoholic extracts of the green leaf, three pronounced absorption bands in the violet region of the spectrum, and are further characterised and distinguishable from one another by giving a different spectroscopic reaction with acid which, in the case of two, is very definite and sensitive. Though spectroscopically there appears to be good evidence of the existence of three distinct colouring matters, yet trying various means I failed to obtain them in the crystalline form or in sufficient state of purity, free from the accompanying fats, etc., to be able to examine their chemical properties, pending which it will, I think, be sufficient to term them for the present L. B. and Y. xanthophyll. They are distributed as follows in the flowers examined:—

|                        |                                                                                                                                                                                                                                                                                                                                                                                              |
|------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| L. xanthophyll.        | Calceolaria, Nasturtium ( <i>Tropæolum</i> ).                                                                                                                                                                                                                                                                                                                                                |
| B. xanthophyll.        | <i>Doronicum</i> (two species), <i>Chrysanthemum</i> ,<br>Charlock ( <i>Raphanus raphanistrum</i> ), Buttercup ( <i>Ranunculus acer</i> ), Sunflower ( <i>Helianthus annuus</i> ), Dandelion ( <i>Taraxacum officinale</i> ),<br>Musk ( <i>Mimulus moschatus</i> ), Laburnum ( <i>Cytisus laburnum</i> ), Coltsfoot ( <i>Tussilago farfara</i> ), Marigold ( <i>Calendula officinalis</i> ). |
| L. and B. xanthophyll. | Wallflower ( <i>Cheiranthus cheiri</i> ).                                                                                                                                                                                                                                                                                                                                                    |
| Y. xanthophyll.        | Tulip, Pansy ( <i>Viola tricolor</i> ), Gorse ( <i>Ulex europæus</i> ).                                                                                                                                                                                                                                                                                                                      |
| L. Y. xanthophyll.     | African Marigold ( <i>Tagetes erecta</i> ), Daffodil ( <i>Narcissus pseudo-narcissus</i> ).                                                                                                                                                                                                                                                                                                  |

Thus, in the above flowers the B. xanthophyll greatly preponderates. In certain varieties of the above, as the dark-coloured calceolaria and wallflower and the various shades of nasturtiums and the red tulip, the xanthophyll is present as usual but is masked by the presence of these additional pigments, which in each case can be removed by extracting with hot water in which they are easily soluble. The depth of colour of the flowers appears to depend upon the amount of pigment present and not upon the particular xanthophyll; thus in the case of the chrysanthemum three different varieties were examined, a very rich yellow, a medium coloured and a very pale one, but in each the pigment consisted of B. xanthophyll. Of the African marigold, three shades of flowers were also examined, varying from a rich orange to a very pale yellow, but the majority of the pigment in each consisted of L. xanthophyll.

The spectra of these three xanthophylls each consist of three bands situated between the solar lines F and H, and compared to chrysophyll and to one another the bands exhibit a gradual shifting towards the violet, those of chrysophyll being the least refrangible and those of Y. xanthophyll the most (Plate 6, figs. 1—5). They form a very similar and closely connected series of spectra, which points to a close relationship between these colouring matters. There is generally an indication in each of a fourth more refrangible band, but this is not apparent in the fresh extracts and I believe is due to spontaneous change which takes place after a time. The photographic plates of their spectra, as well as of chrysophyll, show that the ultra-violet rays are transmitted to a considerable extent, though this visibility is somewhat lost in the reproduction. Though the bands of each occupy different positions in the spectrum, it is by the change brought about in their spectra by the action of acid that these three xanthophylls can be definitely distinguished from one another. In the case of L. xanthophyll HCl has no immediate effect, the bands fading after a time



with an indication of a fourth more refrangible, the solution becoming by degrees paler and assuming a slight green tinge before becoming colourless.  $\text{HNO}_3$  on the other hand rapidly affects the colouring matter, a fourth more refrangible pronounced band is formed, the first and second by degrees disappear and the third becomes faint, the solution in a short time assumes a green tinge and finally becomes colourless (Plate 6, figs. 10—14). The same reaction takes place with  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}_2$ , and nascent H, but with these reagents the action is slower. On the other hand HCl produces an immediate and striking effect upon the spectra of B. and Y. xanthophyll, their solutions at once became paler yellow in colour; in the former the first band disappears the resulting spectrum consisting of three distinct bands, the first two a little less refrangible in position than the original second and third with an indication of a fourth in the ultra-violet at M, while in the latter three pronounced bands are formed, removed considerably towards the violet and ultra-violet with an indication of a fourth at N (Plate 6, figs. 6—9).

The reaction in both cases is a most delicate one, a very small quantity of acid being required, otherwise the reaction takes place too rapidly to be observed. It is evidently due to the formation of two other yellow colouring matters from the B. and Y. xanthophylls, which are, however, unstable in the presence of the acid and are rapidly destroyed, the solution becoming a greenish-blue and finally colourless in a short time. A similar change takes place in these two xanthophylls on standing for a time, the above two colouring matters being formed spontaneously, but under these circumstances they appear to be more or less stable and their alcoholic solutions can be kept for a considerable time without further change taking place.

In the case of some flowers (as coltsfoot and marigold) the extracted pigment appears to be a mixture of B. xanthophyll and the colouring matter formed from it by the action of acid or spontaneous change. Sorby\* has already noticed the formation of this colouring matter from his "yellow xanthophyll" by the action of acids, but the change that the Y. xanthophyll undergoes has not before been noticed I think.  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  produces in both the same effect as HCl, the action being more energetic especially with the latter.

In the separation by carbon-bisulphide the greater portion of the pigment is taken up in the first fraction, the subsequent ones containing less and less and by examining together the spectra of each and the action of HCl one can readily determine which xanthophyll is present. In cases of mixtures of L. and B. and L. and Y., which occur in the wallflower, daffodil and African marigold, the L. being more soluble in carbon-bisulphide than the B. and Y., the latter will be found more or less free from the L. in the subsequent fractions and the action

\* 'Roy. Soc. Proc.,' vol. 21, p. 459.

of HCl will confirm their presence, and so sensitive is the reaction that the admixture of very small quantities of B. and Y. with L. can be easily detected. The alcoholic extract, after the carbon-bisulphide separation, besides containing the yellow colouring matters which are soluble in water and absorb the violet and ultra-violet rays will also contain some xanthophyll, but the bands of the latter are generally so obscured by the former, that only in cases where there is but little obscuration is an examination possible, but a certain amount of clearing up of the spectrum may be effected by adding water and ether, the xanthophylls being more soluble in ether than these colouring matters. If the fatty waxy deposit which, as mentioned before, forms on cooling from the extracts, and is deeply impregnated with pigment be dissolved in alcohol and examined, it will be found to contain the xanthophyll group only and in cases of mixtures to contain the L. xanthophyll free from the B. and Y. which points to the fact that in the presence of fats the former is less soluble in alcohol than the latter.

In contradistinction to the B. and Y. the L. xanthophyll is more or less stable, its alcoholic solutions showing but little change even after the lapse of several weeks when kept away from the light, and is in fact, more stable than chrysophyll under the same conditions. Towards acids,  $H_2O_2$  and nascent H both appear to behave in a very similar manner though chrysophyll withstands the action of HCl to a greater extent. This similarity together with the close resemblance of their spectra, the slight shift in the bands being the only difference, indicates but a slight difference in their chemical constitution, and though in none of the flowers experimented with was any chrysophyll obtained, yet under certain conditions it may be that chrysophyll is elaborated from the L. xanthophyll.

With HCl no colour reaction is produced in alcoholic solutions of chrysophyll and L. xanthophyll, but with the B. and Y. a striking effect is produced. Taking fairly concentrated solutions and adding a little concentrated HCl, after a short time a deep green coloration is produced which changes to peacock blue, purple and then gradually fades, the solutions becoming colourless in a day or two, the reaction being more rapid in the case of the Y. and the colour effect being slightly more brilliant. On the addition of ammonia the original yellow colour though less intense is produced, the blue colour reappearing on acidifying and *vice versa*. Sorby\* mentions this reaction in connection with his "Yellow Xanthophyll," and is, I believe, the first to have noticed it. If the blue solutions be examined spectroscopically, but a faint indication of bands is discernible, but after the addition of alkali the spectra produced by the action of acid upon the B. and Y. xanthophylls are exhibited, so that it appears the action of acid first produces these two yellow colouring matters from the B. and

\* *Loc. cit.*

Y. which under the action of the acid give rise to a blue pigment which is reconverted into them by the addition of alkali and *vice versâ*. The same reaction takes place with  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  but the colour effects are not so brilliant. In the dry state both chrysophyll and L. xanthophyll as well as the B. and Y. turn a Prussian-blue colour with a drop of concentrated  $\text{HNO}_3$  which is evanescent, an indigo-blue with concentrated  $\text{H}_2\text{SO}_4$  which is more lasting, and the two latter assume a green colour with concentrated  $\text{HCl}$ , there being no alteration in colour the two former in this case.

### *Leaves.*

From the concentrated alcoholic extracts of healthy green leaves, as is well known, minute sparkling red crystals having a metallic lustre form in the course of a day or so, and in cases where deposits form from the hot extracts on cooling, the crystals will also be found embedded in it. This substance which appears to be universally present in all green leaves but varying in amount, is the Chrysophyll of Hartsen and Schunck\*, and according to Arnaud† is identical with Carotin, the crystalline substance obtained from the carrot root and which name he applies to it. These minute crystals from the green leaf extracts can be freed from chlorophyll and the other colouring matters present by washing with cold alcohol in which they are almost insoluble and recrystallising from ether in which they are very soluble, and from which this substance crystallises in the form of beautiful red metallic leaflets on slow evaporation. Chrysophyll is also soluble in boiling alcohol and glacial acetic acid, readily soluble in carbon-bisulphide, but insoluble in alkalies. No very definite chemical reactions of this substance so far are known, it is not a stable body and in contact with the air soon decomposes, it can, however, be preserved in an atmosphere of hydrogen without change.  $\text{HCl}$  has no effect upon the crystals, they dissolve, however, in concentrated  $\text{H}_2\text{SO}_4$  producing a deep Prussian-blue solution which soon changes to purple and then brown, and  $\text{HNO}_3$  decomposes them at once. The colour reactions the crystals assume as mentioned above with a drop of concentrated  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  appear to be a general reaction of this group of colouring matters. According to Tschirch‡ who applies to it the name Xantho-Carotin, this substance forms with iodine a green derivative.

The absorption spectrum of three pronounced bands situated between F. and H (Plate 7. fig. 1) appears to be the most characteristic and distinguishable property of chrysophyll which on the addition of a small quantity of  $\text{HNO}_3$  to the alcoholic solution undergoes similar changes to that which L. xanthophyll passes through the bands fading

\* 'Roy. Soc. Proc.', vol. 44, p. 449.

† 'Compt. Rend.', vol. 102, p. 1119, and vol. 104, p. 1293.

‡ 'Berichte der Deutschen Botanischen Gesellschaft,' vol. 14, Part II, p. 84.

without change in position and a fourth more refrangible one being formed, but with Chrysophyll, it is not so pronounced, the solution assumes a greenish tinge and in a short time becomes colourless. The action of  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}_2$  and nascent H appears to be the same, but the action is slower. HCl has a very feeble action, the solution gradually becoming paler in colour without any green tinge, and colourless in a week or two, the three bands gradually fading without the formation of any additional ones. Alkalies have no effect upon the spectrum.

The means whereby the yellow colouring matters accompanying chlorophyll in the alcoholic green-leaf extracts can be separated from the latter, and their subsequent separation by carbon-bisulphide has been the subject of a previous investigation.\* In the light of the results obtained with the flowers it appears now that besides chrysophyll the other xanthophylls present are the L. and B. and the colouring matter formed from the latter by the action of acid, and in addition there are present those yellow colouring matters that cause obscuration in the violet and ultra-violet, and as in flowers vary in amount with the particular plant. In those cases where a fourth band is visible in the spectrum this is due to the acid derivative of B. xanthophyll, the proportion of these two colouring matters varying in different leaves, and the preponderance of one or the other can be decided by the aspect of the spectrum and the action of acid thereon. In the above investigation I considered that the interpretation of the series of spectra obtained by the carbon-bisulphide separation was that the crude xanthophyll extract is a mixture of chrysophyll and what now turns out to be B. xanthophyll and its acid derivative, but in the light of the experiments upon flowers, and further experiments upon the xanthophyll of the leaf taken in comparison, I am of the belief that L. xanthophyll must also be present in order to fully satisfy the spectroscopic observations. The xanthophyll of all leaves appears to be composed of these same components, and where the flower xanthophyll varies, as in the daffodil, wallflower, charlock and tulip, yet their leaf xanthophyll is the same as in other green leaves.

An experiment was made with the yellow pigment of the etiolated leaf of the daffodil compared to the normal green leaf of the same plant, and the xanthophyll in each was found to be the same, save that from the etiolated leaf no chrysophyll crystals were obtained, which were plentiful in the extract from the normal leaf in which the chlorophyll had formed after the etiolated plant had been subjected to the action of sunlight. Lastly, as regards the xanthophyll of the autumnal leaf spectroscopic observation shows the presence of L. xanthophyll, and a great preponderance of the acid derivative of B. xanthophyll over the normal B. xanthophyll, which causes the spectrum to be four-banded in the majority of cases, the chlorophyll no longer being

\* 'Roy. Soc. Proc.,' vol. 68, p. 471.

formed at this season and disappearing, leaving the accompanying xanthophylls which gives the leaf its characteristic autumnal colour.

From these few observations it seems that the formation of chrysophyll within the leaf depends on similar conditions to the elaboration of the chlorophyll, but whether it is formed independently or from one of the xanthophylls present is still a problem to be solved.

*Fruit, etc.*

Several varieties of the orange were examined, and here a considerable amount of the pigment of the rind is soluble in water and causes the great amount of obscuration in the violet and ultra-violet observed in the alcoholic extracts of the pigment. The redness of the rind which is present in many (as the Blood, Seville and Tangerine) appears to be due to these colouring matters, which can be removed by boiling water leaving the rind the normal orange colour. By treating the rind with boiling alcohol a rich orange-coloured extract of the pigment is obtained, from which on cooling a deep orange deposit forms. If this deposit be dissolved in a little absolute alcohol chrysophyll crystals form in a small quantity on slow evaporation. The spectrum of the alcoholic solution of the deposit, which as in the deposits from flowers exhibits no obscuration in the violet and ultra-violet, indicates that besides chrysophyll there are also present the acid derivatives of B. and Y. xanthophyll. The mother liquor of the deposit which contains the majority of the pigment spectroscopically does not show the presence of chrysophyll, indicating that this substance is present in but small quantity, the absorption bands visible after the separation by carbon-bisulphide appearing to be due principally to the acid derivatives of B. and Y. xanthophyll. In the lemon the yellow pigment of the rind consists principally of the colouring matters producing obscuration together with the above acid derivatives.

The crystalline substance obtained from the pigment of the carrot root (*Daucus Carota*) and which is termed Carotin, has been the subject of investigation by Arnaud,\* who considers it a hydrocarbon of the formula  $C_{26}H_{38}$ , though Husemann who has also examined the substance applies that of  $C_{18}H_{24}O$ . I have compared this substance with chrysophyll and find, as with Arnaud, that they have the same properties and that their spectroscopic properties, which he did not examine, are identical save that the bands of carotin appear to be very slightly moved towards the violet as compared to those of chrysophyll (Plate 7, figs. 1 and 2). Towards acids the spectroscopic reaction is identical in each. It may be the slight difference in the positions of the bands is merely due to spontaneous change or oxidation that has

\* 'Compt. Rend.,' vol. 100, p. 751; vol. 102, pp. 1119, 1319; vol. 104, p. 1293; vol. 109, p. 911.

taken place in the carotin while within the root. From the extract of the pigment prepared by boiling the grated root with alcohol, the carotin crystallises out on cooling, but a larger yield is obtained from the juice of the grated root, which contains the majority of the carotin in suspension, from which on drying it can be dissolved in ether and recrystallised in the same form of crystals as chrysophyll. There is a certain amount of those colouring matters present which obscure the violet and ultra-violet, but the majority of the total pigment appears to consist of carotin alone.

The pigment of the tomato (*Lycopersicum esculentum*) is interesting in so much as it consists of a crystalline substance not before described, I believe, and which gives a very characteristic spectrum of similar character to the other xanthophylls and from its reactions appears to be of similar constitution. The tomatoes were first boiled with water which extracted a little yellow colouring matter, the watery extract filtered off and the pulp and skin washed with cold alcohol and the red pigment extracted with boiling alcohol, in which it is not easily soluble and which takes some time to extract the whole. A deep orange-coloured extract is obtained, from which on cooling a rich red deposit forms which is sparingly soluble in alcohol. In ether the deposit dissolves readily, and on slow evaporation deep-red crystalline needles form which can be purified by recrystallising from ether. If the pulp and skin be first dried and the pigment extracted with ether in the cold, which takes some days, the same substance crystallises out on slow evaporation. The crystals are with difficulty soluble in boiling alcohol from which they crystallise out on standing, they are not so soluble in ether as chrysophyll neither have they the metallic lustre of the latter; in alcohol and ether their solutions are orange, but in carbon-bisulphide, in which they are easily soluble, the colour is reddish-pink, due to the shifting of the bands in this solvent considerably towards the red. They dissolve in hot glacial acetic acid giving pale yellow solutions, but spectroscopic examination shows in contradistinction to chrysophyll that this substance is acted upon by the acid during solution, producing another colouring matter similar to that formed by the action of strong acids upon its alcoholic solutions. In alkalis the crystals are insoluble. Like chrysophyll they dissolve in concentrated  $\text{H}_2\text{SO}_4$ , producing a deep Prussian-blue solution which soon changes to purple and then brown.  $\text{HNO}_3$  causes immediate decomposition and  $\text{HCl}$  has no action. With a drop of concentrated  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  the same colour reactions are produced as with chrysophyll. It is not a stable substance, and exposed to the air in the absence of light it is decomposed in the course of a few weeks.

The absorption spectrum is a very distinctive and definite one of three bands considerably less refrangible in position than those of chrysophyll, the first one being situated in the green (Plate 7,

figs. 3 and 4). The first two bands are very intense, the third fainter, there is also a pronounced band a little less refrangible than the solar line N, which is absent in the chrysophyll spectrum and which appears to be less intense in the ethereal solution, though the other bands are of the same intensity and occupy the same positions in the two solvents. As with chrysophylls and the other xanthophylls the ultra-violet rays are transmitted. Spectroscopic observation also shows that this substance constitutes nearly the whole of the pigment present in the tomato, there being evidence of another in small quantities which can be formed from it by the action of acids, but those that obscure the violet and ultra-violet are almost absent. Though its ethereal solutions are fairly stable, a change soon takes place in the alcoholic solutions, the colour changing from orange to yellow and gradually becoming paler, at the same time the bands become fainter and are replaced by three faint ones in the same positions as those of B. xanthophyll. With HCl,  $H_2SO_4$  and  $HNO_3$  a similar change in the spectrum takes place, its alcoholic solutions gradually assuming a pale yellow colour without any decided green tinge and finally colourless. The spectrum produced by the action of acid upon B. xanthophyll is not assumed, thus one cannot say whether the yellow colouring matter which it undoubtedly gives rise to and the gradual formation of which can be traced in the spectrum under the influence of acid, is B. xanthophyll or not. A similar reaction appears to take place with nascent H. Believing that this substance has not been isolated before, or if it has, has been mistaken for carotin, I venture to apply to it the name *Lycopin*.

From the seeds of the annatto (*Bixa Orellana*) Bixin, to which the formula  $C_{28}H_{34}O_5$  has been given, can be obtained by dissolving the annatto of commerce in boiling alcohol, which gives rise to a reddish-brown crystalline mass on evaporation. If this be washed with a little alcohol, dried, and dissolved in boiling glacial acetic acid, the bixin crystallises on cooling and standing in the form of brownish-red leaflets, which are soluble in alcohol, ether and carbon-bisulphide and also in ammonia and sodium hydrate, but insoluble in water. It resembles chrysophyll and lycopin in many respects, dissolving in concentrated  $H_2SO_4$  with a very intense blue colour, which soon changes to purple and finally becomes reddish-brown.  $HNO_3$  likewise decomposes it and HCl has no action even on boiling. The crystals with a drop of  $H_2SO_4$  and  $HNO_3$  turn a brilliant blue with the former and the evanescent Prussian-blue coloration with the latter. Its spectrum resembles chrysophyll save that the three bands which are of the same intensity in each are less refrangible in position, being situated between those of chrysophyll and lycopin, there is no band at N as in the latter, and the ultra-violet rays are transmitted. The alcoholic solution is a rich orange-yellow which fades on the addition of  $HNO_3$ .

without assuming a green tinge, the bands, however, shift slightly towards the red and gradually fade without the formation of any additional ones; the addition of ammonia causes the bands to shift a little towards the violet. It thus appears that bixin is an allied substance to chrysophyll and the other xanthophylls, and as it is stable and more easy to prepare than the other crystallisable members of the group, it may with advantage form a starting point to study the chemical constitution and relationship of the xanthophylls.

*Yellow Pigment of the Egg Yolk and Fowl Serum.*

The above yellow pigment together with that of the serum of other animals, of fats, butter, of the *corpus luteum* of the ovary has been the subject of investigation by Thudichum, Hammarsten, Malay, Krukenberg, MacMunn, Halliburton and others. Thudichum was the first to examine the pigment of the *corpus luteum* and the name Lutein was given to it, which name was extended to the whole group. Krukenberg's word, Lipochrome has, however, generally been adopted by physiologists. As they are characterised by giving bands towards the violet region of the spectrum, and also by the same colour reactions with  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  in the dry state as exhibited by the xanthophylls, a comparison was made between the yellow pigment of the egg-yolk and serum of the fowl and the xanthophyll of flowers. The pigment of the egg-yolk can be extracted by treating the yolk freed from the white with alcohol in excess, which precipitates the proteids which take up the pigment leaving the filtrate colourless. If the precipitate be now treated with hot absolute alcohol, the yellow pigment is dissolved and the separation by carbon-bisulphide applied. In the case of the serum the blood-clot is allowed to stand twenty-four hours, broken up and the serum filtered off; it is of a deep yellow colour but more or less masked by the red corpuscles held in suspension. Alcohol is now added in excess, and the yellow pigment which is carried down by the precipitated proteids is extracted with hot absolute alcohol and the separation by carbon-bisulphide is performed. They both form bright yellow alcoholic solutions and the spectrum of each is identical with that of L. xanthophyll, and from the examination of the crude extracts and the carbon-bisulphide fractions the pigment appears to consist of this colouring matter only, with an almost total absence of those colouring matters that obscure the violet and ultra-violet (Plate 7, figs. 5—7). The action of acids upon the spectra is identical with the action upon L. xanthophyll (Plate 7, figs. 8—13), and the colour reactions in the dry state with  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  are also the same, the blue coloration being not quite so brilliant, which may be accounted for perhaps by the presence of fats. In the case of the egg-yolk an attempt was made to get rid of the fats by saponifica-



tion, after which the pigment was taken up with ether, and on slow evaporation a few vermillion-coloured crystals formed, which gave the same spectrum as before, but the quantity was so small that it could not be definitely decided whether these crystals represented the pigment or were some other substance coloured by it.

Whether the lipochromes from other sources will also prove to consist of the same colouring matter opportunity of investigation has not so far been afforded, but from the spectroscopic properties of the lipochrome in the above cases it appears to be identical with *L. xanthophyll*, and as it thus appears to be present along with both chlorophyll and hæmoglobin an interesting speculation is presented whether this colouring matter, too, is of physiological importance.

#### EXPLANATION OF THE PLATES.

(The solvent in each case is alcohol.)

##### PLATE 6.

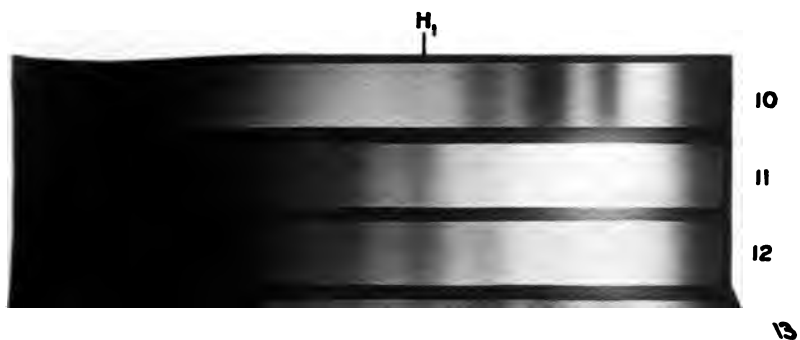
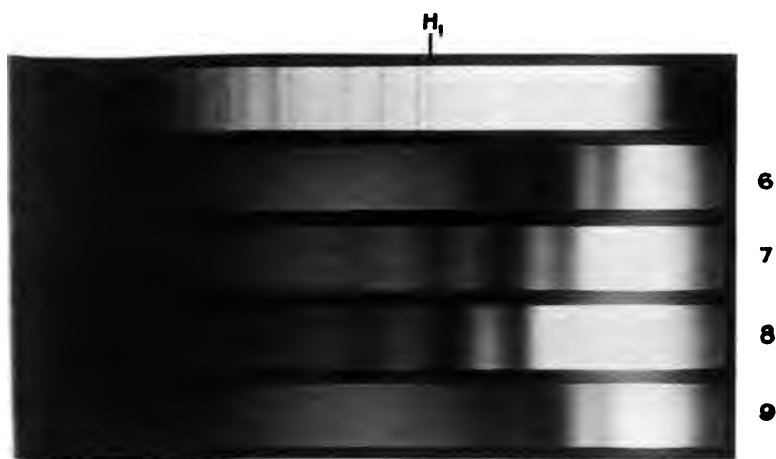
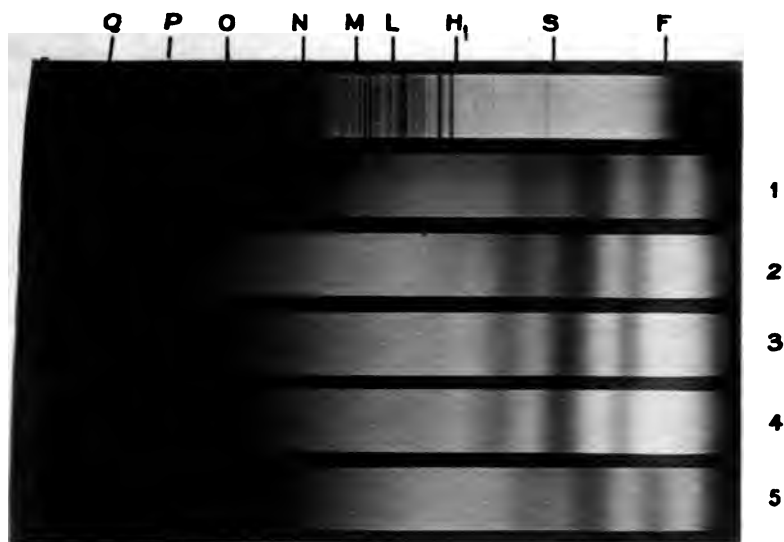
###### Spectra.

- 1 and 5. Chrysophyll from the Daffodil leaf.
2. *L. xanthophyll* from Wallflower.
3. B. " " *Doronicum*.
4. Y. " " Tulip.
6. B. " " *Doronicum*.
7. B. " " " + HCl.
8. Y. " " Tulip + HCl.
9. Y. " " "
10. L. " " Wallflower.
14. L. " " " (stronger solution).
- 13, 12, 11. Action of  $\text{HNO}_3$  upon *L. xanthophyll* of 14, after successive intervals.

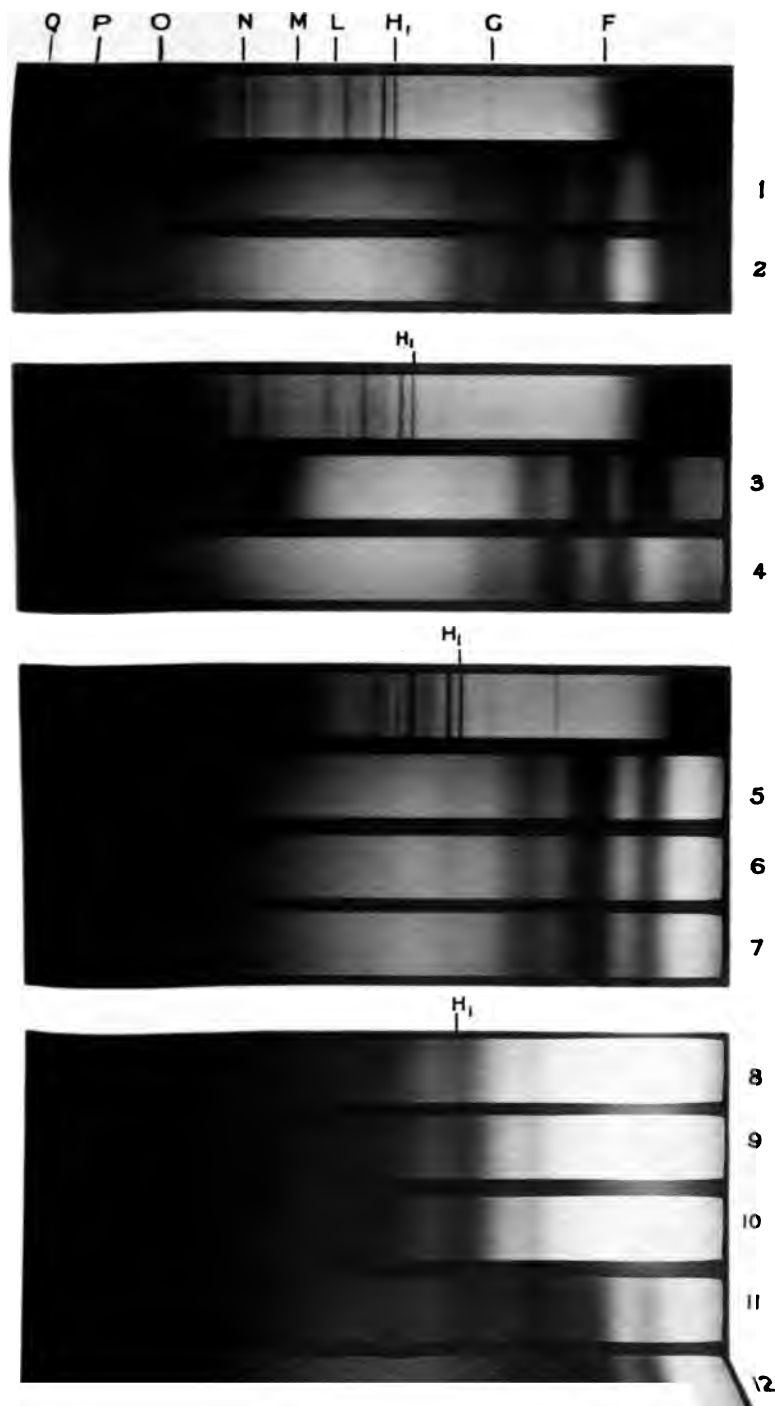
##### PLATE 7.

###### Spectra.

1. Chrysophyll from Spinach.
  2. Carotin from the Carrot.
  3. Lycopin, the colouring matter of the Tomato.
  4. Chrysophyll from Grass.
  5. *L. xanthophyll* from the Nasturtium.
  6. Colouring matter of the Egg-Yolk.
  7. " " " Fowl serum.
  - 11, 12, 13. Action of  $\text{HNO}_3$  upon 5, 6, 7, respectively.
  - 8, 9, 10. " " " " after a further interval.
-









"On the Determination of Specific Heats, especially at Low Temperatures." By H. E. SCHMITZ, M.A., B.Sc. Communicated by ARTHUR SCHUSTER, F.R.S. Received February 2,—Read February 19—Received in revised form June 3, 1903.

The specific heats at low temperatures of various metals have recently been determined by Professor Tilden,\* by U. Behn,† and by C. C. Trowbridge.‡ In the following table are given the values obtained by Tilden and by Trowbridge, and some of the numbers obtained by Behn; the numbers given represent the mean specific heats between the temperature of liquid air or of liquid oxygen and the atmospheric temperature.

|                 | Tilden | Behn   | Trowbridge |
|-----------------|--------|--------|------------|
| Aluminium ..... | 0·1676 | 0·173  | 0·1833     |
| Iron.....       | —      | 0·0853 | 0·0914     |
| Nickel.....     | 0·0838 | 0·0857 | —          |
| Cobalt ..       | 0·0822 | —      | —          |
| Copper .....    | —      | 0·0796 | 0·0868     |
| Silver .....    | 0·0519 | 0·0519 | —          |

The differences in the method of cooling the metal probably furnish a partial explanation of the discrepancies here shown. Tilden used a portable metallic air chamber cooled by means of liquid oxygen, and assumed the initial temperature to be  $-182^{\circ}\cdot 5$ . Behn used a fixed glass air chamber cooled by means of liquid air; the initial temperature was assumed to be that of the liquid air, which was measured by means of a thermo-electric couple. Trowbridge immersed the object directly in liquid air which had been boiling for some time, and assumed the initial temperature to be  $-181^{\circ}\cdot 5$ .

The author of the present paper has made a series of determinations of the specific heats of several metals (i) between the temperature of liquid air and the atmospheric temperature (ii) for the ordinary temperature range,  $100^{\circ}$  to  $20^{\circ}$ . In the former case he has used two distinct methods, one being the method of mixtures. In the latter case he has used only the method of mixtures. The experiments were conducted mainly in the physical laboratory of the Owens College,

\* 'Phil. Trans.,' A, 1900, vol. 194, pp. 246—250.

† 'Wied. Ann.,' 1898, vol. 66, p. 237; also 1900, vol. 1, p. 257.

‡ 'Science,' 1896, vol. 8, p. 6, quoted in 'Science Abstracts,' 1898, No. 1325.

178 Mr. H. E. Schmitz. *On the Determination of* [Feb. 2,  
and the writer has pleasure in expressing his obligations to Professor  
Schuster for advice during the progress of the work.

*Platinum Thermometer.*

The temperature of the liquid air was obtained by means of a Callendar's platinum thermometer with exposed coil, made in accordance with instructions kindly given to the author by Mr. J. E. Petavel. It was found that, when the instrument was placed in a narrow test-tube containing the last remains of a quantity of liquid air made some time before, its resistance went up to a maximum at which it remained practically constant until nearly all the liquid air had evaporated. The steady maximum obtained on several occasions in this way was taken as the resistance at  $-182^{\circ}5$ , which (disregarding the variation with pressure) is very nearly the temperature of liquid oxygen. This value, together with the resistances at  $0^{\circ}$  and  $100^{\circ}$ , enabled Callendar's formula to be used. The lowest observed temperature of the liquid air obtained in this way was  $-191^{\circ}0$ .

*Calorimeter for Method of Mixtures.*

The inner vessel was of very thin brass or copper. Different quantities of water were used, as shown in the following list:—

| Calorimeter | Apparent weight<br>of water | Total<br>water-equivalent |
|-------------|-----------------------------|---------------------------|
|             | Grammes                     | Grammes                   |
| A.....      | 70.0                        | 73.8                      |
| B.....      | 200.0                       | 203.7                     |
| C.....      | 400.0                       | 405.1                     |
| D.....      | 550.0                       | 562.2                     |
| E.....      | 700.0                       | 712.8                     |

In each case the vessel was nearly full of water, and the thermometer was immersed to a constant depth. The water equivalent of the thermometer bulb (from the mass of water displaced) was 0.9 gramme; the water equivalent of the whole immersed portion was estimated at 1.5 grammes.

*Mercury Thermometer.*

This was one of Goetze's Beckmann thermometers. It was carefully compared with a secondary standard of which the calibration corrections were known; in the final comparison the readings were taken at every tenth of a degree in a very slowly rising temperature. As a

result of the comparison it appeared that the relation between the Beckmann scale and the corrected scale of the secondary might be taken as linear throughout. In obtaining the value of a degree on the Beckmann in terms of a degree on the secondary standard, it was found necessary to exercise considerable care, as the observed values for the ice-point of the secondary varied between  $0^{\circ}61$  and  $-0^{\circ}04$  according to its previous state. The temperature  $t$  of the secondary was accordingly calculated from the reading  $T_t$  in accordance with the equation  $t = 100 (T_t - T_0^t) / (T_{100} - T_0^{100})$ .\* One degree on the Beckmann (kept, as regards the amount of mercury in the bulb, in a constant state during all except the earliest experiments) was found to be equal to  $1^{\circ}009$  on the secondary standard.

The value of the Beckmann degree was however more satisfactorily ascertained by comparison with a Baudin thermometer, No. 12772, the corrections for which are very accurately known from the work of Schuster and Gannon.† The comparison was made at two points, distant each about half a degree from one of the extremities of the Beckmann scale. A considerable number of readings were taken in the neighbourhood of each of the two points; all were rejected except those which indicated in the case of each thermometer a very slowly rising temperature. The corrections of the Baudin for calibration and unequal division, though small, were relevant. The only other correction requiring consideration was that for stem temperature. Since in the specific heat determinations no correction for the exposed part of the Beckmann (scale-length  $5^{\circ}$ ) is applied, the uncorrected Beckmann should be compared with the corrected Baudin. The Baudin was exposed from division 12, and the temperatures of comparison were approximately  $15^{\circ}$  and  $19\frac{1}{2}^{\circ}$ . On the range of  $4\frac{1}{2}^{\circ}$ , the correction for exposed stem might possibly approach 1 part in 1000, but would probably be much less than this. Disregarding the stem correction, the following values were obtained for the Beckmann degree in terms of the Baudin degree, 1.0101, 1.0117, 1.0110, 1.0086, 1.0093, 1.0103, 1.0113, 1.0109, 1.0111, 1.0110, mean 1.0105. Making an allowance for the stem correction, this has been called 1.011. To reduce an interval  $t_B$  on the Baudin (used vertically) to the corresponding interval  $t$  on the French hard-glass scale, the following relation has been given by Schuster and Gannon,  $t = t_B (1 - .00135)$ . The Beckmann degree is therefore equivalent to  $1.010^{\circ}$  on the French hard-glass scale of the mercury thermometer. The results which follow are expressed in the first instance in terms of the French hard-glass scale. An interval on this scale lying between  $14^{\circ}$  and  $20^{\circ}$  is reduced to the scale of the

\* 'Phil. Trans.,' A, 1895, p. 428.

† 'Phil. Trans.,' A, 1895, p. 432, *et seq.*, also 'Owens College Book of Standards.'



hydrogen thermometer by subtracting  $0.003^{\circ}$  per degree ; this reduction is made use of in Table IV.

The absolute value of the Beckmann reading was given with sufficient accuracy by the comparison with the secondary standard. The correction was approximately  $+14.55$  at the lower extremity of the Beckmann scale and  $+14.60$  at the upper extremity.

#### *Specific Heat of Water.*

The specific heat of water at  $17.5$  has been taken as unity, as recommended by Griffiths. In all except a few of the earlier of the experiments on copper, it was not necessary to apply a correction for variation of the specific heat of water ; where necessary, the correction was made by means of the values given by Griffiths, "Thermal Measurement of Energy," Table VII.

#### *Method of Cooling the Metal.*

Experiments were made with a view to finding a satisfactory method of cooling the metal in an air chamber, surrounded or partly surrounded by liquid air, but these were not successful. The method of direct immersion in the liquid air was therefore adopted. This method has the disadvantage that a certain quantity of liquid air adheres to the body after its extraction from the bath ; this, if carried into the calorimeter, causes an error of more or less importance. Again, it is possible that the temperature of the body may *fall* slightly after its withdrawal from the bath, owing to the rapid evaporation of liquid air from its surface ; a marked effect of this kind was observed in the case of the platinum thermometer, but in this case the mass was small and the surface large ; in the experiments described below this effect is probably negligible.

#### *Copper.*

A number of preliminary experiments on pieces of copper of various shapes led the author to the conclusion that the error, caused by the adhesion of liquid air, would be comparatively small if the piece of metal were massive in comparison with its surface. The amount of liquid air entering the calorimeter may moreover be materially lessened by shaking the piece of metal during its transference from the bath of liquid air to the calorimeter. Thus a cylinder of copper, suspended in the bath with its axis vertical, gave, in two experiments in which it was rapidly and steadily transferred to the calorimeter,  $0.0815$  and  $0.0811$  for the apparent specific heat. On the other hand, *when it was shaken during a transference lasting about 5 seconds, it gave in two experiments*  $0.0801$  and  $0.0799$ . It will presently appear

that the difference between these numbers and the previous numbers is not, or is not in the main, due to variation in the time of transference. The effect of a variation in the time of transference is shown in Table I. This table gives the results of fourteen experiments on a copper cylinder, the time of transference being varied from experiment to experiment. The cylinder here used was not the same as that to which the previous numbers refer; it was however cut from the same casting of pure copper. It was made with a conical upper end, so that it might be the less able to carry liquid air on its upper surface; its edges also were rounded off. It was always slightly shaken during the transference.

On graphical examination of the numbers in Table I, it appeared that if the relation between time and apparent specific heat in Experiments 8 to 14 be assumed linear, then the apparent specific heat in Experiments 1 to 7 is on the average slightly greater than that given

Table I.

| Number<br>of experiment | Time of<br>transference in<br>seconds | Apparent<br>specific heat |
|-------------------------|---------------------------------------|---------------------------|
| 1                       | 1                                     | 0·08025                   |
| 2                       | 2                                     | 0·0798                    |
| 3                       | 3                                     | 0·0806                    |
| 4                       | 4                                     | 0·0794                    |
| 5                       | 5                                     | 0·0799                    |
| 6                       | 7½                                    | 0·0797                    |
| 7                       | 10                                    | 0·0797                    |
| 8                       | 15                                    | 0·0795                    |
| 9                       | 20                                    | 0·0784                    |
| 10                      | 30                                    | 0·0783                    |
| 11                      | 40                                    | 0·0774                    |
| 12                      | 60                                    | 0·0762                    |
| 13                      | 80                                    | 0·0742                    |
| 14                      | 120                                   | 0·0724                    |

Table II.

| Number<br>of experiment | $x$ | 10,000 $y$ | 10,000 $\Delta$ |
|-------------------------|-----|------------|-----------------|
| 1                       | 1   | 800·7      | +1·8            |
| 2                       | 2   | 800·0      | -2·0            |
| 3                       | 3   | 799·3      | +6·7            |
| 4                       | 4   | 798·7      | -4·7            |
| 5                       | 5   | 798·0      | +1·0            |
| 6                       | 7½  | 796·3      | +0·7            |
| 7                       | 10  | 794·6      | +2·4            |

Table II.—*continued.*

|    |     |       |       |
|----|-----|-------|-------|
| 8  | 15  | 791.3 | + 3.7 |
| 9  | 20  | 787.9 | - 3.9 |
| 10 | 30  | 781.2 | + 1.8 |
| 11 | 40  | 774.5 | - 0.5 |
| 12 | 60  | 761.1 | + 0.9 |
| 13 | 80  | 747.7 | - 5.7 |
| 14 | 120 | 720.9 | + 3.1 |

by the line representing the results of Experiments 8 to 14. This would be explained by supposing that in Experiments 1 to 7, or in some of them, some of the liquid air had not been got rid of by shaking and entered the calorimeter. From later work it appeared that anomalous results, such as those of Experiments 3 and 4, were probably due more to a chance variation in the amount of liquid air carried over than to other errors of experiment.

In Table II the numbers of Table I are reduced according to the following plan:—Experiments 8 to 14 are represented by the equation  $y = c - mx$ , where  $y$  is the apparent specific heat for time of transference  $x$ . The method of least squares gives  $c = 0.080135$ ,  $m = 0.0000671$ . Table II gives the values of  $y$  for Experiments 1 to 7 as well as for Experiments 8 to 14, and in the last column the differences between these numbers and the numbers in Table I.

The mean of Experiments 1 to 5 (Table I) is 0.0800, which differs but little from the value of  $c$  above, and is adopted by the author as representing the specific heat of copper, the principle being that the small amount of liquid air, not got rid of by shaking during a short transference, approximately compensates for the heating effect of the atmosphere during the transference. Results for other metals were obtained on the same principle. As a standard shape for the specimens, a short cylinder with approximately hemispherical ends was adopted where possible. The number in brackets after each result for the specific heat of a given metal indicates the time of transference in seconds. This time was generally 3 or 5 seconds; it was in general found that any difference between a result for 3 seconds and a result with the same piece of metal for 5 seconds was covered by the experimental errors. Five seconds was found to be a more convenient time than three, allowing for a more deliberate treatment and greater uniformity of shaking.

The mercury thermometer was read to 0°.001, the temperature observations being made in accordance with the following scheme:—

Reading of platinum thermometer.

Period of  $2\frac{1}{2}$  minutes, with readings of mercury thermometer at end of every half-minute.

Interval of  $2\frac{1}{2}$  minutes, reading of platinum thermometer during the interval.

Period of  $2\frac{1}{2}$  minutes, with readings of mercury thermometer at end of every half-minute.

Immersion of object in calorimeter (half a minute after the last reading).

Period of  $7\frac{1}{2}$  minutes, with readings of mercury thermometer at end of every half-minute.

Interval of  $2\frac{1}{2}$  minutes.

Period of  $2\frac{1}{2}$  minutes, with readings of mercury thermometer at end of every half-minute.

The first ten readings of the mercury thermometer gave the initial rate of change of temperature and also the temperature at the moment of immersion; the last ten gave the final rate of change. The final temperature was obtained as the mean of the later of the corrected intermediate readings. It was found that equilibrium of temperature was attained in about 3 minutes in the case of the copper cylinder of Tables I and II. The weight of this cylinder was approximately  $161\frac{1}{2}$  grammes; calorimeter D was used, and the fall of temperature was approximately  $4^{\circ}6$ .

The initial readings were always made with a falling temperature, but this circumstance did not seem to introduce any important uncertainty. During the final readings the temperature was sometimes rising, sometimes falling.

The copper used was obtained from Johnson, Matthey and Co., and described as pure.

#### *Thallium.*

The original object of the investigation was to determine the specific heat of this metal, but as the amount used was small, the experimental error is here probably larger than in the case of the other metals. The first specimen examined weighed about 30 grammes. After forming the material into a single mass, approximately cubical, it gave in two experiments 0.0299 (4) and 0.0298 (4) for the specific heat. A second specimen, of nearly double the weight of the first and similarly molten and compressed into a compact mass, gave 0.0298 (4) and 0.0301 (3). The two specimens together gave 0.0302 (4), 0.0300 (3), 0.0301 (3), mean 0.0301. Calorimeter B was used, and the fall of temperature in the last three experiments was approximately  $2^{\circ}5$ .

The first specimen was from Dr. Schuster, the second was bought as pure. An analysis of the second specimen by Mr. Joseph Race gave thallium 99 per cent., oxygen (probably due to surface oxidation of the fragments analysed) 1 per cent., traces of iron and zinc.

*Lead.*

A specimen supplied by Johnson, Matthey and Co., of a purity of about 99.9 per cent., gave 0.02942 (3), 0.02933 (4), 0.02936 (5), 0.02924 (7), mean of the first three 0.0294. Mass of lead approximately 250 grammes, calorimeter C, fall of temperature approximately 3°.6.

Table III gives the results of ten experiments on commercial sheet lead. The object of these experiments was to test the comparability of the results when the mass and also the proportion of surface to mass was varied. The shapes of the specimens are given in Table VI. All the calorimeters made use of in the investigation were included in this series of experiments, with the secondary object of testing the comparability of results obtained with different calorimeters.

Table III.

| Calorimeter | Mass of lead | Approximate fall of temperature | Specific heat |
|-------------|--------------|---------------------------------|---------------|
|             | Grammes.     |                                 |               |
| A .....     | 35.06        | 2°.8                            | 0.0294 (5)    |
| B .....     | 64.51        | 1.9                             | 0.0293 (5)    |
| B .....     | 129.3        | 3.8                             | 0.0292 (5)    |
| B .....     | 140.9        | 4.1                             | 0.0292 (5)    |
| C .....     | "            | 2.1                             | 0.0292 (5)    |
| C .....     | 246.3        | 3.6                             | 0.0292 (5)    |
| C .....     | 285.8        | 4.2                             | 0.0294 (5)    |
| D .....     | 246.3        | 2.8                             | 0.0298 (5)    |
| D .....     | 285.8        | 3.0                             | 0.0293 (5)    |
| E .....     | "            | 2.4                             | 0.0293 (5)    |

Five further experiments with the piece of lead of mass 285.8 grammes, using calorimeter C, gave 0.0295 (3), 0.0296 (3), 0.02945 (3), 0.0295 (4), 0.02945 (5). Mean result for sheet lead 0.02935. An analysis by Mr. Race showed lead 99.5 per cent., tin 0.13 per cent., traces of iron, copper and antimony.

*Aluminium.*

A specimen supplied by Johnson, Matthey and Co., was analysed by Mr. Race and found to contain 98 per cent. of aluminium, 1 per cent. of zinc, 0.7 per cent. of iron, small quantities of silica, etc. It gave in the first instance in two experiments 0.1725 (4), 0.1733 (5). For these experiments the piece of metal had been only roughly trimmed in the lathe. As a comparatively large quantity of liquid air was evidently, in these two experiments, carried into the calorimeter, the piece of metal was reshaped with a very smooth surface. It now gave 0.1731 (3), 0.1721 (4), 0.1721 (5), mean 0.1724. Mass of aluminium approximately

72 grammes, calorimeter E, fall of temperature approximately  $3^{\circ}5$ . In the second set of experiments the amount of liquid air entering the calorimeter was distinctly less than in the first; the inference, therefore, that may be drawn from the approximate identity of the results in the two sets of experiments is that in neither case was the amount of liquid air calorimetrically of much consequence.

A commercial casting gave, after a rough trimming in the lathe 0.153 (3), 0.154 (3), and, after a final shaping and smoothing, 0.153 (3), 0.1525 (3). Mass (in the second pair of experiments) approximately 88 grammes. An analysis by Mr. Race showed aluminium 88 per cent., zinc 7 per cent., copper 4 per cent., the balance lead, iron, silica, etc., with a trace of nickel. The specific heat found is much lower than would be indicated by this analysis and Regnault's law of mixtures.

#### *Iron.*

A ball of cast-iron, mass approximately  $110\frac{1}{2}$  grammes, gave in two experiments 0.0897 (3), 0.0889 (5). These experiments were made merely for comparison with the results given by the ice method described later.

#### *Nickel.*

A specimen supplied by Johnson, Matthey and Co., was found by Mr. Race to contain nickel and cobalt 98.5 per cent. (cobalt approximately 0.9 per cent.), iron 0.6 per cent., copper 0.7 per cent., some silica. It gave 0.0848 (5), 0.0842 (5), 0.0840 (5), mean 0.0843. Mass approximately 192 grammes, calorimeter E, fall of temperature approximately  $4^{\circ}5$ .

#### *Cobalt.*

A specimen supplied by Johnson, Matthey and Co., was found by Mr. Race to contain cobalt and nickel 97.5 per cent. (nickel 0.5 per cent. approximately), iron 1.9 per cent., small quantities of copper, lead, carbon and a trace of zinc. It gave 0.0843 (5), 0.0846 (5), 0.0841 (5), mean 0.0843. Mass approximately 165 grammes, calorimeter E, fall of temperature approximately  $3^{\circ}9$ .

#### *Zinc.*

A specimen of Dr. Mond's metal, supplied by Johnson, Matthey, and Co., gave 0.0838 (3), 0.0839 (4), 0.0840 (5), mean 0.0839. Mass approximately 169 grammes, calorimeter E, fall of temperature approximately  $4^{\circ}0$ .

A second specimen, nominally pure, gave 0.0849 (5), 0.0854 (5). Mass approximately 71 grammes. In this specimen Mr. Race found 99.7 per cent. zinc, no trace of any other metal.

A commercial casting gave 0.0835 (3), 0.0835 (5). Mass approximately 106½ grammes. Mr. Race found 99.5 per cent. zinc, a small quantity of tin, traces of arsenic, copper, lead, aluminium.

#### *Silver.*

A specimen of bar silver, supplied by Elkington and Co., was found by Mr. Francis Jones to contain silver 98.06 per cent., gold 0.17 per cent., the balance being at least partly copper. It gave 0.05133 (5), 0.05147 (5), 0.05129 (5), mean say 0.0514. Mass approximately 176 grammes, calorimeter C, fall of temperature approximately 4°.5.

#### *Tin.*

A specimen supplied by Johnson, Matthey and Co., practically pure, gave 0.04993 (3), 0.04973 (4), 0.04963 (5), mean say 0.0498. Mass approximately 173 grammes, calorimeter E, fall of temperature approximately 2°.4. An additional experiment, calorimeter C, gave 0.04997 (5).

A commercial specimen gave 0.0502 (3), 0.0503 (3), 0.05001 (5), 0.04997 (5). Mass approximately 130 grammes. In this case the casting contained numerous small air-holes, and was only roughly trimmed in the lathe. A considerable amount of liquid air was carried into the calorimeter, and this probably makes the results a little too high. Mr. Race found tin 99.3 per cent., lead 0.45 per cent., traces of iron and zinc.

#### *Summary.*

In Table IV are collected the results already given. For comparison Behn's numbers are added in the last column.

Table IV.

| Metal                         | Specific heat |                |        |
|-------------------------------|---------------|----------------|--------|
|                               | Mercury scale | Hydrogen scale | Behn   |
| Copper, pure .....            | 0.0800        | 0.0798         | 0.0796 |
| Thallium, approx. pure .....  | 0.0301        | 0.0300         | —      |
| Lead, pure .....              | 0.0294        | 0.0293         | 0.0296 |
| Lead, commercial .....        | 0.02935       | 0.0293         | —      |
| Aluminium, approx. pure ..... | 0.1724        | 0.1719         | 0.173  |
| Aluminium, commercial .....   | 0.153         | 0.152          | —      |
| Cast iron .....               | 0.0893        | 0.0890         | —      |
| Nickel, approx. pure .....    | 0.0843        | 0.0840         | 0.0857 |
| Cobalt, approx. pure .....    | 0.0843        | 0.0840         | —      |
| Zinc, pure .....              | 0.0839        | 0.0836         | 0.0842 |
| Zinc, approx. pure .....      | 0.085         | 0.085          | —      |
| Zinc, commercial .....        | 0.0835        | 0.083          | —      |
| Silver, approx. pure .....    | 0.0514        | 0.0512         | 0.0519 |
| Tin, pure .....               | 0.0498        | 0.0497         | 0.0501 |
| Tin, commercial .....         | 0.050?        | 0.050?         | —      |

*Ice Method.\**

When an object cooled by means of liquid air is plunged in water, a firm coating of ice is rapidly formed. If the water is not stirred, the ice remains unmelted for a considerable time. This suggested the weighing of the ice as a possibly practical method of determining the specific heat of the material. After a number of preliminary experiments, it was found that the method was capable of yielding very consistent results. Thus five experiments were made with a ball of commercial zinc weighing  $106\frac{1}{2}$  grammes, giving the following numbers:—

| Initial temperature | Mass of ice | Specific heat |
|---------------------|-------------|---------------|
|                     | Grammes     |               |
| -185°·8             | 20·74       | 0·0838        |
| -182°·6             | 20·39       | 0·0838        |
| -190°·0             | 21·26       | 0·0840        |
| -186°·4             | 20·85       | 0·0840        |
| -184°·6             | 20·56       | 0·0836        |

The calorimeter contained water kept at very nearly 0° C. by means of an ice jacket, and the time of immersion in the calorimeter in each of the above experiments was five minutes. The initial temperature was deduced from the reading of a platinum thermometer observed  $\frac{1}{4}$  or  $\frac{1}{2}$  minute before extracting the object from the bath of liquid air. After removal from the calorimeter, the object was transferred to a vessel in which the ice was dried by contact with filter-paper cooled by means of melting ice, and was finally transferred to another vessel in which the ice was weighed. The number assumed for the latent heat of water is 80·0, this appearing to the author the best value he could take for the purpose of reducing his results to the unit used in the preceding part of the investigation.

The method appeared to offer advantages in its comparative simplicity and in its avoidance of thermometrical difficulties, and the author felt encouraged to attempt an extended examination of the method, with a view to the estimation of the relative importance of the sources of error. He here selects the more important considerations.

(i) An object which carries a quantity of liquid air on its upper surface, for instance, a cylinder with axis vertical, may by the method

\* [Note added 27th May, 1903.—The author has learned that the method of weighing an ice-jacket is not new. It was briefly described by Joly in 'Nature,' 1895, vol. 52, p. 80, and was subsequently independently invented and used by Dewar. See also a paper by Bedford and Green, 'B. A. Report,' 1901, p. 544, in which is described a calorimeter resembling in some of its features that used by the author.]



of mixtures give appreciably too high a result if the liquid air is allowed to enter the calorimeter. But in this method the corresponding error will probably be of trifling amount, as the bulk of the liquid air rises to the surface of the water immediately on immersion of the object in the calorimeter; it sometimes forms independent ice capsules floating on the water. There is no necessity from this point of view to attach much importance to the time of transference from the bath of liquid air to the ice calorimeter.

(ii) A minute quantity of liquid air is always vaporised in contact with the object, or in its immediate proximity, and is imprisoned within the ice coating. This causes the chief difficulty in the method as practised by the author. The difficulty arises, not from any calorimetrical effect, but from the fact that the vaporised air slowly and gradually escapes in small bubbles through one or more holes near the top of the ice coating, its place being taken by water drawn in some way into the interior of the ice coating and therefore necessarily weighed with the ice.

(iii) For the reason mentioned in the last paragraph, the shape as well as the size of the immersed object is of importance. The object should be large and should have a small surface. Its base should be well rounded, otherwise a bubble of air of considerable size may form at the base in the earliest stages of the formation of the ice coating; this may produce a large error in the manner above described.

(iv) On account again of the gradual suction of water into the ice coating, the result depends on the time of immersion in the calorimeter.

The statements of the three preceding paragraphs are illustrated by Tables V and VI. In Table V each of the numbers given is the mean of three, four, five or six. In Table VI the results of the

Table V.—Variable Immersion.

|                           | Flat-ended<br>copper cylinder,<br>101·15 grammes | Copper sphere,<br>62·49 grammes | Copper cylinder<br>with rounded<br>base,<br>161·57 grammes |
|---------------------------|--------------------------------------------------|---------------------------------|------------------------------------------------------------|
|                           | Apparent sp. h.                                  | Apparent sp. h.                 | Apparent sp. h.                                            |
| Immersion of 3 to 6 mins. | 0·0798                                           | 0·0800                          | 0·0790                                                     |
| Immersion of 10 mins. ... | 0·0818                                           | 0·0816                          | 0·0800                                                     |
| Immersion of 15 mins. ... | 0·0816                                           | 0·0815                          | 0·0801                                                     |
| Immersion of 30 mins. ... | 0·0837*                                          | 0·0829                          | 0·0817                                                     |

\* This number is not quite comparable with the others in the table. In the experiments of which it gives the mean result, the calorimeter was in a more efficient state than in the other long-period determinations.

Table VI.—Constant Immersion of Five Minutes.

| Mass<br>of Lead | Shape, &c.                                              | Approximate mass<br>of ice<br>(apparent) | Apparent specific heat |        |
|-----------------|---------------------------------------------------------|------------------------------------------|------------------------|--------|
|                 |                                                         |                                          | Exp. 1                 | Exp. 2 |
| Grammes         |                                                         | Grammes                                  |                        |        |
| 35·06           | Cube, fine wire ring for suspension                     | 2·6                                      | 0·0316                 | 0·0323 |
| 36·29           | Sphere ditto                                            | 2·6                                      | 0·0309                 | 0·0304 |
| 37·36           | Sphere, flange for suspension ..                        | 2·7                                      | 0·03145                | 0·0305 |
| 64·51           | Flat-ended short cylinder, axis<br>vertical, wire ..... | 4·8                                      | 0·0319                 | 0·0317 |
| 129·3           | Cylinder as before, but of twice<br>the length .....    | 9                                        | 0·0309                 | 0·0306 |
| 140·9           | Sphere, flange.....                                     | 10                                       | 0·0304                 | 0·0303 |
| 246·3           | Short cylinder, with rounded<br>ends, flange.....       | 17                                       | 0·0303                 | 0·0304 |
| 285·8           | Plummet, with tapering rounded<br>base, wire .....      | 20                                       | 0·0303                 | 0·0303 |

individual experiments are given. The material in the case of Table V is pure copper; the three objects described were cut from the same casting. In the case of Table VI the material is commercial sheet lead; all the objects described were made from the same sample.

The numbers in Table V might at first sight be supposed to indicate that the process of formation of the ice coating is a very slow one, and is not complete in less than half-an-hour. The author was led to reject this hypothesis after weighing the object with its ice coating during immersion. It will be sufficient to describe a single experiment on the copper sphere of  $62\frac{1}{2}$  grammes. The first observation was made two minutes after plunging the sphere in the calorimeter. The apparent weight rapidly decreased at first, indicating additional formation of ice. After a very short time the apparent weight began to increase, and continued to increase during the remainder of the hour during which the experiment was continued. The observed increase in apparent weight divided itself into two parts: (1) There was a very slow and nearly uniform increase due to the gradual melting of the coating of ice; (2) there was an occasional relatively large increase due to the escape of a bubble of air.\* From this and similar experiments the author concluded that the formation of ice might, in the case of the objects used by him, be considered as being practically complete in 5 minutes or less. The rate of melting in the experiment quoted was 3 per cent. of the total mass per hour; the calorimeter, however, was of a less efficient form than that finally adopted.

\* The presence of the enclosed air made it useless to attempt to deduce the weight of ice from the apparent weight in water.

The last six results in Table VI are in good agreement with one another, but are in excess of the result given by the method of mixtures. The author has no doubt that the difference is due to the water imprisoned in the ice coating.

Table VII exhibits the results of a final series of experiments by the ice method. These experiments were conducted so far as possible in a uniform manner, differing slightly from that previously employed. The time of transference was about 5 seconds, and during the transference the piece of metal was well shaken. The time in the calorimeter was approximately 5 minutes, the time in the drying apparatus  $\frac{1}{2}$  minute. In the case of nickel the ice-coated cylinder was too large for the drying apparatus, and was dried by hand.

Table VII.

| Metal                 | Mass<br>of Metal | Approximate mass<br>of ice | Apparent specific<br>heat |         | Specific<br>heat<br>by mixture<br>(from<br>Table IV)* |
|-----------------------|------------------|----------------------------|---------------------------|---------|-------------------------------------------------------|
|                       |                  |                            | Exp. 1.                   | Exp. 2. |                                                       |
| Copper, pure .....    | Grammes 161.6    | Grammes 30                 | 0.07945                   | 0.0792  | 0.0800                                                |
| Lead, pure .....      | 250.4            | 18                         | 0.0299                    | 0.0301  | 0.0294                                                |
| Aluminium, approx. p. | 72.4             | 29                         | 0.1724                    | 0.1746  | 0.1724                                                |
| Nickel, approx., pure | 192.3            | 37                         | 0.0826                    | 0.0820  | 0.0843                                                |
| Cobalt, approx., pure | 165.0            | 32                         | 0.0840                    | 0.0833  | 0.0843                                                |
| Zinc, pure .....      | 169.3            | 34                         | 0.0849                    | 0.0850  | 0.0839                                                |
| Silver, approx., pure | 176.2            | 22                         | 0.0519                    | 0.0520  | 0.0514                                                |
| Tin, pure .....       | 172.9            | 21                         | 0.0507                    | 0.0510  | 0.0498                                                |

*Specific Heats for the Range 20° to 100°.*

In view of the uncertainty prevailing as to the effect on specific heat, not only of impurities, but also of physical state in respect of hardness and density, the author regarded it as of importance to determine the specific heats at ordinary temperatures of the actual specimens used in the low temperature determinations. He used the method of mixtures, the procedure being, so far as the different circumstances permitted, the same as in the low temperature determinations by the method of mixtures. It was necessary in this case to make the time of transference as short as possible. After numerous preliminary trials, the arrangement finally adopted was a fixed steam-heater

\* In comparing the two methods, it should not be forgotten that the ranges of temperature are not the same. The specific heat given by the ice method is for the range  $-185^{\circ}$  to  $0^{\circ}$ , while that given by the method of mixtures is for the range  $-185^{\circ}$  to  $+15^{\circ}$ .

standing a few inches above a fixed calorimeter, the latter protected from the direct radiation of the former (except during the short time occupied in transferring the hot body to the calorimeter) by a screen of metal and wood forming the base of the heater. The hot body could be very rapidly lowered into the calorimeter, probably without appreciable cooling. A chief cause of uncertainty appeared to lie in the temperature of the hot body; this was read on a thermometer with its bulb very near the body, but there was no doubt that the thermometer acquired the temperature of the surrounding hot air much more rapidly than did the comparatively massive piece of metal. To eliminate this source of error, the heating process was generally continued for 3 or 4 hours, and in certain cases for 6 hours.

The thermometer used in the steam-heater was graduated in tenths of a degree from  $95^{\circ}$  to  $105^{\circ}$ , the length of a degree on the scale being approximately 24 mm. It had been examined at Kew, but the corrections actually applied were obtained by the frequent use of the hypsometer, which showed during the determinations a progressive rise in the steam-point amounting altogether to  $\frac{1}{4}^{\circ}$ .

In the calorimeter a Beckmann thermometer was used. It was convenient in many of the experiments to use a different instrument from that used in the low temperature determinations. This second instrument was carefully standardised in the same manner as the first, but unfortunately proved to have a bore far from uniform. The results obtained with it are those for copper (all), thallium (both), aluminium approx. pure (first result), aluminium commercial (both), nickel (both), zinc approx. pure (both).

The quantity of water used was 200, 300 or 400 grammes, and the rise of temperature  $1^{\circ}\cdot1$  (thallium) to  $5^{\circ}\cdot6$  (nickel).

Table VIII gives the results of all the experiments made with the exception of the following: (1) preliminary tests of the method, made with copper, thallium, lead commercial, zinc commercial; (2) one experiment with lead pure, result 0.0301, rejected on the ground of probably insufficient time of heating; (3) one experiment with tin commercial, result 0.0551, rejected on the ground of an unduly long transference.

#### *Dulong and Petit's Law.*

In Table IX the specific heats of Tables IV and VIII are compared. The metals are here arranged in order of atomic weight. The atomic heats, calculated from the international atomic weights (oxygen 16) for 1903, are added. So far as the metals examined are concerned, the table shows that the proportional alteration of specific heat is relatively large for metals of low atomic weight. Hence the approximate constancy of atomic heat for the higher temperature range is not preserved for the lower temperature range. In fact for the lower

temperature range, the metals examined show a progressive rise of atomic heat with atomic weight.

Table VIII.

| Metal                      | Specific heat (hydrogen scale) |         |          |
|----------------------------|--------------------------------|---------|----------|
|                            | Exp. 1                         | Exp. 2  | Mean     |
| Copper, pure .....         | 0·0941                         | 0·0941  | } 0·0936 |
| Ditto .....                | 0·0940                         | 0·0929  |          |
| Ditto .....                | 0·0936                         | 0·0936  |          |
| Ditto .....                | 0·0933                         | 0·0932  |          |
| Thallium, approx. pure.... | 0·0825                         | 0·0827  | 0·0826   |
| Lead, pure .....           | 0·08044                        | 0·08048 | 0·08046  |
| Lead, commercial .....     | 0·08069                        | 0·08058 | 0·0806   |
| Aluminium, approx. pure    | 0·2182                         | 0·2183  | 0·21825  |
| Aluminium, commercial..    | 0·1917                         | 0·1914  | 0·19155  |
| Cast iron.....             | 0·1190                         | 0·1188  | 0·1189   |
| Nickel, approx. pure.....  | 0·1093                         | 0·1095  | 0·1094   |
| Cobalt, approx. pure.....  | 0·1080                         | 0·1079  | 0·10795  |
| Zinc, pure. ....           | 0·0934                         | 0·0928  | 0·0931   |
| Zinc, approx. pure.....    | 0·0947                         | 0·0938  | 0·09425  |
| Zinc, commercial.....      | 0·0911                         | 0·0913  | 0·0912   |
| Silver, approx. pure ..... | 0·05595                        | 0·05594 | 0·0559   |
| Tin, pure .....            | 0·05524                        | 0·05522 | 0·0552   |
| Tin, commercial.....       | 0·05495                        | 0·05514 | 0·0550   |

Table IX.

| Metal                      | Specific heat for mean temperature : |        | Ratio of specific heats | Atomic heat for mean temperature : |       |
|----------------------------|--------------------------------------|--------|-------------------------|------------------------------------|-------|
|                            | - 85°                                | + 60°  |                         | - 85°                              | + 60° |
| Aluminium, approx. pure..  | 0·172                                | 0·218  | 0·79                    | 4·66                               | 5·91  |
| Aluminium, commercial..    | 0·152                                | 0·192  | 0·79                    | —                                  | —     |
| Cast iron.....             | 0·0890                               | 0·119  | 0·75                    | —                                  | —     |
| Nickel, approx. pure.....  | 0·0840                               | 0·1094 | 0·77                    | 4·93                               | 6·42  |
| Cobalt, approx. pure.....  | 0·0840                               | 0·108  | 0·78                    | 4·96                               | 6·37  |
| Copper, pure .....         | 0·0798                               | 0·0936 | 0·85                    | 5·08                               | 5·95  |
| Zinc, pure. ....           | 0·0836                               | 0·0931 | 0·90                    | 5·47                               | 6·09  |
| Zinc, approx. pure.....    | 0·085                                | 0·094  | 0·90                    | —                                  | —     |
| Zinc, commercial.....      | 0·083                                | 0·091  | 0·91                    | —                                  | —     |
| Silver, approx. pure ..... | 0·0512                               | 0·0559 | 0·92                    | 5·53                               | 6·03  |
| Tin, pure .....            | 0·0497                               | 0·0552 | 0·90                    | 5·91                               | 6·57  |
| Tin, commercial.....       | 0·050 ?                              | 0·0550 | 0·91 ?                  | —                                  | —     |
| Thallium, approx. pure.... | 0·0300                               | 0·0326 | 0·92                    | 6·12                               | 6·65  |
| Lead, pure .....           | 0·0293                               | 0·0305 | 0·96                    | 6·06                               | 6·31  |
| Lead, commercial .....     | 0·0293                               | 0·0306 | 0·96                    | —                                  | —     |

*Note on the Specific Heat of Aluminium, added May 27, 1903.*—A specimen of aluminium from the British Aluminium Company of an approximate purity of at least 99½ per cent., gave in three experiments 0·2194, 0·2185, 0·2194, mean 0·2191, as the specific heat between 20° and 100°.

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“The Elasmometer, a New Interferential Form of Elasticity Apparatus.” By A. E. H. TUTTON, F.R.S. Received May 12,—  
Read May 14, 1903.

(Abstract.)

Being desirous of extending the investigation of the physical characters of the crystals of isomorphous salts to the subject of their elasticity, the question arose as to the best form of apparatus to employ for the determination of the coefficient of elasticity. The most accurate form hitherto devised is that of Koch\*. The amount of flexure of a thin plate of the crystal was determined by the interference method, sodium light being employed. The great convenience and high accuracy of the optical part of the interference dilatometer which the author has described to the Royal Society†, suggested the advantage of utilising it as interferometer for the measurement of the amount of the flexure of the plate, and many other possible improvements on the apparatus of Koch also suggested themselves. Eventually the instrument now described was devised. It has been constructed by Messrs. Troughton and Simms.

The observing telescope, with its auto-collimator and attached hydrogen Geissler tube, is exactly as used for the dilatometer, and its pedestal is mounted on a detachable plinth in front of the elasmometer. The rigid iron base on which the latter is mounted also accommodates, on its back portion, the pedestal of the vertical tube which carries the train of prisms to select the monochromatic C—or F—hydrogen light employed, and direct it on the interference apparatus. The interference chamber of the dilatometer is detached from the lower end of this tube, as the elasmometer carries its own interference tripod.

The elasmometer proper consists of the following seven essential parts:—

(1.) A pair of platinum-iridium wedges, arranged parallel to each other and with the knife-edges downwards, up against which the plate of the substance (not necessarily a crystal) is to be bent by a weight applied under its centre. They are carried by a pair of gunmetal

\* ‘Ann. der Phys.,’ N.F., 1878, vol. 5, p. 251.

† ‘Phil. Trans.,’ A, vol. 191, p. 313.

blocks, which are adjustable as to their distance apart, and are suitably recessed at their inner ends to accommodate the wedges and the plate-supporting and weight-applying apparatus. They slide on a very rigid larger block of steel, mounted to the front and left of the centre of the iron base, and one of them is provided with fine adjustments for altitude and azimuth, to enable the knife-edges to be set exactly parallel.

(2.) A pair of mechanical "fingers," for supporting the plate and adjusting it in the proper position under the knife-edges, and for eventually pressing it up into just full contact with the latter. They are carried by a fitting to the left side of the steel block, and terminate in little spring tables each carrying a small gunmetal knife-edge above its inner side. They are adjustable for separation, height, and their position in or out of the recess.

(3.) A delicate balance, by Oertling, of special construction, at one end of whose beam the bending weight is applied through an upright agate point, the pressure-point, which is carried instead of a pan at this end. The balance is mounted to the right of the steel block on a strong base, which is movable by rack and pinion so that the pressure-point can be exactly centred under the plate, and a fine adjustment for azimuth is also provided in the mounting of the balance to aid in this object. A pan at the right-hand end of the beam receives the bending weight, which may amount to 500 grams., and a counterpoise for the weight of the pan is provided near the left end.

(4.) A transmitter, for conveying the bending movement of the centre of the plate to the interference apparatus. It takes the form of a T-piece, whose long stem is horizontal and is fitted with an agate wedge, by which it rests on an agate plate carried on the front block, and a counterpoise; the lower end of the vertical crosspiece rests with less than 1 gram. of pressure on the centre of the plate, while its upper end terminates in a black glass disc, which is adjustable above a metallic one so as to bring its polished surface truly horizontal. This surface is the lower one of the two which reflect the interfering light.

(5.) An interference tripod for supporting the large colourless glass disc whose under surface forms the upper of the two surfaces concerned in the interference. One screw is mounted on the back block, and two screws are carried on the front block; the stem of the transmitter passes between these latter, and the black glass surface is only separated from the colourless disc by a film of air of the necessary thickness to allow for its diminution, consequent on the bending of the plate, without contact of the surfaces.

(6.) A measuring microscope, wherewith to determine the dimensions of the plate and to find its centre. It is mounted to the left of the steel block, and its two rectangular measuring movements read to a thousandth of a millimetre by a novel direct method, involving the

use of a single screw in each case fitted with a special device to eliminate back-lash.

(7.) A control apparatus, to enable the observer to modify at will the rapidity with which the bending force is applied, so as to adequately retard the transit of the interference bands and permit of their easy counting. It depends on an exceedingly fine vertical screw, which carries under a bracket at its head an agate plate arranged above a platinum-iridium control-point, similar to the pressure-point, carried on a saddle of the beam midway between the latter and the central fulcrum wedge. The screw is rotated by a diminishing gear, so that a movement of the lever handle manipulated by the observer to the extent of 3 cm. corresponds to the transit of a single band.

To prevent flickering of the bands when the control is removed and the whole weight allowed to play, due to earth tremors or other disturbances, an aluminium disc is attached below the balance pan by a short rod and immersed in cedar oil, a platinised counterpoise being added to that for the pan already on the other side. The slight viscosity of this oil scarcely diminishes the sensibility of the balance, while its resistance to the vertical movement of the horizontal disc renders the bands absolutely steady for the determination of their position when the weight is fully operative.



"On the Spectrum of the Spontaneous Luminous Radiation of Radium at Ordinary Temperatures." By Sir WILLIAM HUGGINS, K.C.B., O.M., D.C.L., Pres. R.S., and Lady HUGGINS. Received July 17, 1903.

## [PLATE 8.]

The discovery of an element possessing such remarkable and novel properties as radium, which in its separate and distinct form as a new chemical element we owe to the researches of Professor and M<sup>d</sup>me. Curie, has already thrown many beams of suggestive light into the very obscure regions of the constitution of matter. In radium we have a body which appears to be spontaneously and without ceasing giving off energy in several forms. According to Professor Rutherford,\* following upon the work of Becquerel, M. and M<sup>d</sup>me. Curie, and others, the emanations going off from radium are at least of three kinds. First, an emanation of heavy corpuscles, larger in mass than the hydrogen atom, moving with a high velocity, and carrying a positive charge; secondly of negatively charged electrons which form a powerful and penetrating cathode emanation;† and further, of a radioactivity which diffuses from the radium as if gaseous in its nature. In addition, M. and M<sup>d</sup>me. Curie have found that radium spontaneously maintains a temperature about 1°·50 C. above the surrounding temperature, and therefore emits heat radiations of wave-lengths falling within the infra-red part of the spectrum.

Now, in addition to these forms of radiant energy, the glowing of radium in the dark shows that it emits a luminous radiation spontaneously at ordinary temperatures. It appeared to us probable that in this glow we had not to do with either phosphorescence or fluorescence as usually understood, but with an independent and continuous radiation set up by those more active molecules which are supposed, in consequence of a condition of internal instability, to be the source of all the phenomena of radioactivity, and which can scarcely fail themselves to be violently agitated, in connection with disruptive molecular changes—especially the flinging off of the heavy corpuscles—during which, part of the energy stored up within the molecule is liberated in the kinetic form.

\* 'Phil. Mag.,' April and May.

† As an illustration of the penetrative power of the radio-active effects of pure radium bromide, the following experience may be recorded here. About 1 centigramme of radium bromide (Buchler & Co., Brunswick) had been placed in an upper drawer of my writing table, while in a lower cupboard of the same table was a store of photographic plates. After a week or two, all the plates, in boxes lying upon each other three or four deep, were found to be as completely fogged as if they had been exposed to light.

Taking this view of the luminous radiations visible to the eye, it seemed highly probable that the molecular motions by which they were set up, whether we suppose all the radium molecules alike to be concerned, or those only which are in active change, would be so far analogous to the vibrations produced artificially, when radium vapour is rendered luminous in a flame, or by the blow of an electric discharge, as, in like manner, to set up radiations of certain definite wave-lengths or, in other words, to furnish a spectrum of bright lines.

A preliminary prismatic examination of the glow from pure radium bromide was attempted by eye. In consequence of the feebleness of the light under dispersion a slit spectroscope could not be used. A thin fragment of some length of radium was selected, which in the dark shone as a narrow line of light; when this was viewed through a direct-vision prism, it was seen to be dispersed into a spectrum which extended from the blue down to about D where it became too faint to be traced farther in the direction of the red. Within this faint spectrum certain spots were distinctly brighter, due, in all probability, to the presence of bright lines at those positions in the spectrum.

The success of this preliminary observation encouraged us to hope that it might be possible by availing ourselves of the accumulative power of continuous photographic exposure, to obtain a record of the blue, violet, and ultra-violet regions of the spectrum, if the glow radiations extended so far.

We made use of a small quartz spectroscope which had been constructed some years ago for very faint celestial objects. It consists of a compound quartz prism of  $60^\circ$ , consisting of two prisms of  $30^\circ$  of right-handed and left-handed quartz respectively. The quartz lenses are of short focus and of large angular aperture, being about  $\frac{1}{3}$  f. The focal length of the lenses is  $5\frac{1}{4}$  inches; they are plano-convex, the marginal parts of the convex surfaces being "figured" to diminish spherical aberration.

The solid radium bromide was placed at about a millimetre distance in front of the slit, which had to be wider than if a bright object was being photographed; the width was about  $\frac{1}{160}$ th inch. In the case of the spark spectrum of radium and the comparison spectrum of nitrogen, a slit of less than half this width was used.

With an exposure of 24 hours, faint traces of two lines were seen on the plate. After several trials the negative reproduced on the accompanying plate was obtained with an exposure of 72 hours. The reproduction is enlarged two and a-half times. The spectrum consists of eight bright lines, and at least eight faint lines, together with a faint trace of continuous spectrum in the blue region, which does not come out in the reproduction.

It was seen at once that the two very strong characteristic rays of the spark spectrum of radium, in this part of the spectrum, namely,

3814.5 and 3649.6\* were not present on the plate. It was clear that the spectrum was not that of the radium molecule when excited by the electric discharge. It was indeed not improbable that if the radiation came alone from the most active molecules, which were suffering loss by material emanations, then if we may accept the analogy from sound, like a filed tuning-fork they would no longer give radiations of the same wave-lengths as before.

As soon as measures were taken of the lines it was found that several of them agreed in position within the uncertainty of the measures with lines in the spectrum of helium, but not with the most characteristic helium lines in this part of the spectrum. Now Rutherford and Soddy had pointed out† the almost invariable presence of helium in minerals containing uranium. It seemed, therefore, not impossible that we might have to do with helium contained within the radium bromide, and that this gas was being liberated in connection with the active molecules in a state of molecular vibration, analogous to that set up in gaseous helium by an electric discharge.

In consequence of the wide slit and the small scale of the spectrum, it is not possible to measure with certainty to the fourth figure, but the probable error is, we think, not greater than two units in the fourth place, that is  $\pm 0.0002$ .

[Received August 5.—Further examination of the new spectrum, stimulated by the unsatisfactory fact that the strongest lines of helium were not represented in the spectrum from radium bromide, has shown, quite unexpectedly, that if the new spectrum were slightly shifted relatively to the scale, then the seven strongest lines would agree not only in position, but also in relative intensity and character, with bands of the spectrum of nitrogen.

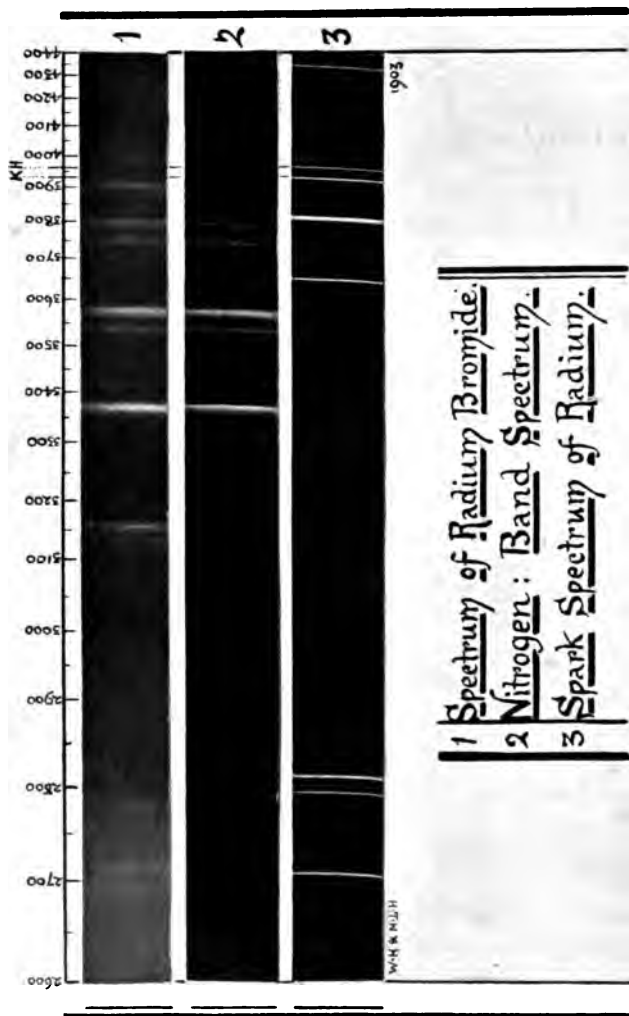
Now, the wave-lengths of the new spectrum had been found from a fiducial comparison solar spectrum, taken on the same plate. The slit is furnished with three shutters, of which the middle one only was open during the long exposure to the radium bromide. When the exposure was over, the middle shutter was closed, and the two side shutters opened, while the spectroscope was directed for a fraction of a second to the sky. As in both cases the collimator lens was filled with light, it was concluded that the wave-lengths would be correct. It is true that the spectroscope had to be placed in a different position for exposure to the sky, but as the instrument is very short and strongly constructed, it was not considered possible that any shift from flexure could arise.

The agreement with the bands of nitrogen is so complete that

\* For spark spectrum of radium, see Demarçay, 'Comptes Rendus,' vol. 129, p. 786, and vol. 131, p. 258; Exner and Haschek, 'Wien. Akad. Sitzber,' vol. 110, July, 1901; Runge, 'Astroph. Journ.,' vol. 12, p. 1.

† 'Phil. Mag.,' 1902, p. 582, and 1903, pp. 453 and 579.

# Spectrum of Radium Bromide





111

though we are unable to trace any cause of shift, we feel justified in shifting the new spectrum on the diagram so as to bring the lines into agreement with those of nitrogen. The amount of shift at the position of the strongest line is nine tenth-metres, which, on the photographic plate, corresponds to the space of  $\frac{1}{100}$ th of an inch.

The positions of the three bands are, according to Ames,\* 3576·85, 3371·2 and 3158·9.

Indications of other lines, besides those which can be seen in the reproduction, can be faintly glimpsed on the negative. There seems little doubt that with a longer photographic exposure a more complete spectrum will be obtained. We have now secured some radium bromide prepared by the *Société Centrale de Produits Chimiques*, and it is our intention to take photographs of this salt, as well as photographs of the German salt, with longer exposures. It may then be, that indications of helium, and possibly of radium itself, may be forthcoming.

Nearly the whole of the ultra-violet radiations appear to come from nitrogen, and we think it best to refrain from any discussion at this moment. Have we to do with occluded, or with atmospheric nitrogen? The remarkable fact should be pointed out that in radium we have a body which at the ordinary temperature, sets up radiations which are similar to those which have hitherto only been obtained in connection with the electric discharge.

*Description of the Plate.*—At the top, is placed a scale of approximate wave-lengths. Immediately below is a reproduction, enlarged two and a-half times, of the spectrum obtained from the radium bromide with an exposure of 72 hours. As has been already explained this has been shifted to bring the lines into position with those of nitrogen photographed from a vacuum tube. The identity of the two spectra seems complete. The third band is faint in the nitrogen spectrum on account of the absorption of the glass of the tube.

Below, is a spark spectrum of radium bromide from the *Société Centrale de Produits Chimiques*. The H and K lines of calcium are present, as well as faintly some of the stronger lines of barium. The characteristic lines of radium at 3814·59 and 3649·7 come out strongly, as well as the strong line recorded by Demarçay at 4340·6. A strong line about 2710 was placed by Berndt† at 2708·6. The strong line a little beyond, about 2814, is due to radium. We do not recognise several lines recorded by Exner and Haschek‡ in this part of the spectrum.]

\* 'Phil. Mag.,' vol. 30, p. 57, 1890. See also Deslandres, 'Comptes Rendus,' vol. 101, p. 1256; and Percival Lewis, 'Astroph. Journ.,' vol. 12, p. 8.

† 'Phys. Zeitschr.,' vol. 2, No. 12 (1900—1901).

‡ 'Sitzb. Ak. Wiss. Wien,' vol. 110, July 4, 1901.

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"On the Oxidising Action of the Rays from Radium Bromide as shown by the Decomposition of Iodoform." By W. B. HARDY, F.R.S., Caius College, Cambridge, and Miss E. G. WILLCOCK, Newnham College, Cambridge. Received July 21, 1903.

In the course of certain experiments one of us noticed that a solution of crystals of pure iodoform in chloroform rapidly became purple. The colour change is due to the liberation of iodine, and the purple solution readily gives the starch test, and is decolourised by thiosulphate. This decomposition of iodoform occurs in a variety of solvents, namely, in chloroform, benzene, carbon bisulphide, carbon tetrachloride, pyridene, amyl alcohol, and ethylic alcohol. In alcohol the change is shown only by a deepening of the original yellow tint of the solution to brown; iodine when dissolved in alcohol having a yellow-brown tint.

As the reaction itself seems not to have been described, a few words may be devoted to it before passing to the main point—namely, the influence of the rays from radium upon this chemical change.

The liberation of the iodine needs the presence of oxygen—though exceedingly minute amounts are sufficient—and some form of radiant energy. When oxygen is washed out by a stream of  $\text{CO}_2$ , or the vapour of the solvent, no change takes place; the solution of iodoform retains its faint yellow tint in full daylight.

If a minute quantity of oxygen be left behind, the colour deepens in daylight to a brownish-yellow, but iodine is not liberated—the solution will not give the starch test. That is to say, there is an intermediate stage of chemical change which is reached in presence of minute amounts of oxygen, and which falls short of the actual liberation of iodine.

If a pair of platinum electrodes be dipped in a solution which is in process of changing to purple, and a field ( $\pm 4$  volts per centimetre) be established, a heavy, oily, colourless liquid slowly drips from each electrode. The nature of this liquid has not yet been determined, but from its specific gravity probably it is methylene iodide.

In the complete absence of any radiant energy, and in presence of abundant oxygen, the solution of iodoform undergoes no change at ordinary temperatures. When heated to near the boiling point, however, the solutions change even in the dark.

Salts, when present, have a remarkable influence on the reaction, although they can hardly be said to be soluble in the reagents employed. For instance, if a solution of iodoform in benzene be divided into two parts, and to one part solid sodium chloride be added, and then both be heated, the one with the salt decomposes much more rapidly. Compared in this way, it was found that

NaCl ; KCl ;  $\text{KNO}_3$  ;  $\text{Pb}(\text{NO}_3)_2$  ;  $\text{Ba}(\text{NO}_3)_2$  ;  $\text{BaCl}_2$  accelerate  
 $\text{K}_2\text{SO}_4$  ;  $\text{CaCO}_3$  ;  $\text{BaSO}_4$  ;  $\text{MgCO}_3$  retard.

It is remarkable that the salts which were tried should so group themselves that those with univalent acids accelerate, those with bivalent acids retard.

The influence of salts appears to be purely a case of surface action. If the salt first be heated for a few minutes with two changes of the solvent (benzene), it entirely loses its power.\*

Probably owing to obscure catalytic action of this kind one finds that in certain apparently clean test-tubes the very sensitive solution of iodoform in chloroform changes to purple even in the dark. The catalysing power of such a tube, however, is very rapidly exhausted.

Probably also owing to catalytic action some samples of iodoform decompose when dissolved in chloroform even in complete darkness. The impurity which brings about this apparently spontaneous change can be distilled off by suspending the sample in water and boiling for a considerable time. The first distillate condenses as a red liquid, when this ceases to come over the distillate will be found to be approximately or quite stable. The impurity can be got rid of more effectively by recrystallising from ethylic alcohol.

The chemical feature on which we wish to lay most stress is that for the liberation of iodine oxygen is needed—it is in all probability due to an oxidation, and, like many oxidation processes, it is carried on, under ordinary circumstances and at ordinary temperatures, only in the presence of light.

The reaction, on the one hand, is a delicate test for the presence of oxygen, on the other, a convenient method for measuring the chemical activity of various rays. We found the trace of oxygen which remains after  $\text{CO}_2$  has been bubbled through the chloroform, and over the iodoform for one hour, sufficient to produce a decisive change of tint.

The beautiful purple colour which the liberated iodine makes in solvents other than alcohol, lends itself readily to measurements which may be made by choosing some solution of iodine in chloroform as a standard colour and matching the fluids under examination with it.

The reaction, when once started, continues for a time in absolute darkness and then ceases. Thus, if light be allowed to play upon a tube so as to produce, say, a faint purple tint, and the tube then be removed to the dark, the faint purple tint will deepen to a certain extent. On renewed exposure to light the action recommences.

\* According to Würster ('Ber. d. Deut. Chem. Gesellschaft,' vol. 19, p. 3201), finely powdered bodies in general occlude "active" oxygen. The two carbonates, however, were the most finely powdered of the salts used.



*Action of the Radiations from Radium.*

We used 5 milligrammes of pure radium bromide, supplied by Buchler & Co., of Brunswick, and we found that a solution of iodoform in chloroform was turned deep purple by simply resting the test-tube containing it on a plate of mica covering the radium salt. That is to say, the active rays penetrate mica and glass.

They also penetrate cardboard. Tubes containing a solution of iodoform in chloroform were enclosed in a box of black cardboard, and they remained unchanged for 60 hours. On placing the box over the radium salt the tubes became purple in about 10 minutes.

For the following reasons we believe that the active rays from radium are entirely different from the active rays of light.

The active rays of sunlight are completely arrested by an opaque layer of lamp-black deposited over a test-tube, by black cardboard, by aluminium, or, in short, by any substance opaque to visible light rays. The active radium rays traverse lamp-black, black cloth, or cardboard, and aluminium sheet 1 mm. thick, without any measurable loss.

An ordinary yellow gas-light was found to emit active rays in quantity sufficient to change iodoform dissolved in chloroform at 1 foot distant in a few minutes, even when the test-tube was jacketed with water in order to prevent any heating. There is, therefore, no reason to believe that the activity associated with light is different from the ordinary chemical activity of light.

The radium rays which produce the change were identified by measuring the effect of screens upon the time necessary to produce a standard depth of purple in 1 c.c. of a standard solution of iodoform in chloroform.

A comparison of radium unscreened and screened so as completely to intercept the  $\alpha$  rays, failed to show any action on the part of these rays.

Attention was then turned to the more penetrating  $\beta$  and  $\gamma$  rays. A corked test-tube was suspended at a constant distance from the radium (approximately 3 mm.), the same test-tube being used throughout. 1 c.c. of the standard solution was used for each measurement. In these measurements the wall of the test-tube was always present as a screen.

Time necessary to read the standard colour—

|                                                    | Minutes.        |      |      | Means. |
|----------------------------------------------------|-----------------|------|------|--------|
|                                                    | 13              | 12   | 13   |        |
| 1. Radium uncovered .....                          | 13              | 12   | 13   | 12·6   |
| 2. Thin screen of mica.....                        | 11              | 12·5 | 12   | 11·8   |
| 3. " " and sheet of writing paper ..               | 12              | —    | —    | 12·0   |
| 4. Glass, $\pm$ 0·5 mm. ....                       | 15              | 14·5 | 14·5 | 14·8   |
| 5. Aluminium, $\pm$ 1 mm. thick .....              | 15·5            | 15·5 | 15·5 | 15·5   |
| 6. Lead plate, $\pm$ 2 mm. thick .....             | between 200—250 |      |      | 225·0  |
| 7.* Four lead plates, each $\pm$ 2 mm. thick ..... | less than 1000  |      |      | <1000  |

\* In this case the distance between the radium and the solution was, of course, increased in order to make room for the screens.

Professor Rutherford was good enough roughly to measure the stopping power of the screens actually used. Nos. 2, 3, 4, and 5 stopped all the  $\alpha$  rays. No. 6 stopped 80 per cent. of the  $\beta$  rays, and allowed the  $\gamma$  rays to pass. No. 7 stopped practically all the  $\beta$  rays, and allowed only  $\gamma$  rays to pass.

The obvious conclusion from these figures is that the action is mainly due to the  $\beta$  rays—that is to say, to the stream of negative electrons. On the other hand, the fact that action is not arrested by as many as four of the lead screens makes it certain that the very penetrating  $\gamma$  rays also are chemically active.

As the  $\gamma$  rays are said to be the same as the Röntgen rays—that is to say, ethereal pulses—the action of the latter was tried by exposing tubes of iodoform dissolved in chloroform, which were enclosed in light-tight cardboard boxes. The Röntgen rays were found to be active, the solutions were purple at the end of 15 minutes.

An exact comparison of the relative activity of light, radium rays and Röntgen rays cannot be attempted, but the experiments prove that light is the most active. The difference appears to be very great. The profound and often lethal physiological action of radium rays must therefore, for the present, be looked upon as being due to their power of penetration rather than to the fact that they exert any novel or very intense action. They reach parts which are shielded by a cuticle very impervious to light waves. Viewed in this way the pigmentation of the human skin found in tropical races, and in those exposed to sunlight, may be regarded as an increased protection to the internal structures which acts by increasing the opacity of the epidermis.

One of us has already shown that the  $\alpha$  rays profoundly modify the *physical* state of colloidal solutions.\* If the colloid particles be electrically negative, the  $\alpha$  rays act as coagulants; if the colloid particles be electrically positive they act as solvents, that is to say, the rays decrease the average size of the particles.

As a provisional basis for investigating the physiological action of radium rays we may therefore regard the  $\alpha$  rays as altering the physical state of the living matter, the  $\beta$  and  $\gamma$  rays as altering the chemical processes, especially perhaps the oxidation processes of the tissues.

It may be well to mention briefly the instances of chemical decomposition produced by radium rays which have been described up to the present.

Berthelot† gives the following cases. Iodic acid is decomposed with liberation of iodine by rays from radium and by light. Unlike the liberation of iodine from iodoform the change proceeds very slowly, free iodine being present only after 14 days' exposure. Nitric acid

\* 'Journal of Physiology,' vol. 29, 1903, p. xxix.

† 'Comptes Rendus,' vol. 133, 1901, p. 659.

204 Sir W. Ramsay and Mr. F. Soddy. *Radioactivity* [July 28, forms nitrous fumes when acted upon by the radium rays or by light.

Becquerel\* mentions the case of mercuric chloride which in presence of oxalic acid is decomposed by light rays, and by radium rays.

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“Experiments in Radioactivity, and the Production of Helium from Radium.” By Sir WILLIAM RAMSAY, K.C.B., F.R.S., and FREDERICK SODDY, M.A. Received July 28, 1903.

1. *Experiments on the Radioactivity of the Inert Gases of the Atmosphere.*

Of recent years many investigations have been made by Elster and Geitel, Wilson, Strutt, Rutherford, Cooke, Allen, and others on the spontaneous ionisation of the gases of the atmosphere and on the excited radioactivity obtainable from it. It became of interest to ascertain whether the inert monatomic gases of the atmosphere bear any share in these phenomena. For this purpose a small electroscope contained in a glass tube of about 20 c.c. capacity, covered in the interior with tin-foil, was employed. After charging, the apparatus if exhausted retained its charge for thirty-six hours without diminution. Admission of air caused a slow discharge. In similar experiments with helium, neon, argon, krypton, and xenon, the last mixed with oxygen, the rate of discharge was proportional to the density and pressure of the gas. This shows that the gases have no special radioactivity of their own, and accords with the explanation already advanced by these investigators that the discharging power of the air is caused by extraneous radioactivity.

Experiments were also made with the dregs left after liquefied air had nearly entirely evaporated, and again with the same result; no increase in discharging power is produced by concentration of a possible radioactive constituent of the atmosphere.

2. *Experiments on the Nature of the Radioactive Emanation from Radium.*

The word emanation originally used by Boyle (“substantial emanations from the celestial bodies”) was resuscitated by Rutherford to designate definite substances of a gaseous nature continuously produced from other substances. The term was also used by Russell (“emanation from hydrogen peroxide”) in much the same sense. If the adjective “radioactive” be added, the phenomenon of Rutherford is distinguished from the phenomena observed by Russell.

\* *Ibid.*, vol. 133, 1901, p. 709.

In this section we are dealing with the emanation, or radioactive gas obtained from radium. Rutherford and Soddy investigated the chemical nature of the thorium emanation\* and of the radium emanation,† and came to the conclusion that these emanations are inert gases which withstand the action of reagents in a manner hitherto unobserved except with the members of the argon family. This conclusion was arrived at because the emanations from thorium and radium could be passed without alteration over platinum and palladium black, chromate of lead, zinc dust, and magnesium powder, all at a red-heat.

We have since found that the radium emanation withstands prolonged sparking with oxygen over alkali, and also, during several hours, the action of a heated mixture of magnesium powder and lime. The discharging power was maintained unaltered after this treatment, and inasmuch as a considerable amount of radium was employed it was possible to use the self-luminosity of the gas as an optical demonstration of its persistence.

In an experiment in which the emanation mixed with oxygen had been sparked for several hours over alkali, a minute fraction of the total mixture was found to discharge an electroscope almost instantly. From the main quantity of the gas the oxygen was withdrawn by ignited phosphorus, and no visible residue was left. When, however, another gas was introduced, so as to come into contact with the top of the tube, and then withdrawn, the emanation was found to be present in it in unaltered amount. It appears, therefore, that phosphorus burning in oxygen and sparking with oxygen have no effect upon the gas so far as can be detected by its radioactive properties.

The experiments with magnesium-lime were more strictly quantitative. The method of testing the gas before and after treatment with the reagent was to take  $\frac{1}{20000}$ th part of the whole mixed with air, and after introducing it into the reservoir of an electroscope to measure the rate of discharge. The magnesium-lime tube glowed brightly when the mixture of emanation and air was admitted, and it was maintained at a red heat for three hours. The gas was then washed out with a little hydrogen, diluted with air and tested as before. It was found that the discharging power of the gas had been quite unaltered by this treatment.

The emanation can be dealt with as a gas; it can be extracted by aid of a Töpler pump; it can be condensed in a U-tube surrounded by liquid air; and when condensed it can be "washed" with another gas which can be pumped off completely, and which then possesses no luminosity and practically no discharging power. The passage of the emanation from place to place through glass tubes can be followed by

\* 'Phil. Mag.,' 1902, p. 580.

† *Ibid.*, 1903, p. 457.

the eye in a darkened room. On opening a stopcock between a tube containing the emanation and the pump, the slow flow through the capillary tube can be noticed; the rapid passage along the wider tubes; the delay caused by the plug of phosphorus pentoxide, and the sudden diffusion into the reservoir of the pump. When compressed, the luminosity increased, and when the small bubble was expelled through the capillary it was exceedingly luminous. The peculiarities of the excited activity left behind on the glass by the emanation could also be well observed. When the emanation had been left a short time in contact with the glass, the excited activity lasts only for a short time; but after the emanation has been stored a long time the excited activity decays more slowly.

The emanation causes chemical change in a similar manner to the salts of radium themselves. The emanation pumped off from 50 milligrams of radium bromide after dissolving in water, when stored with oxygen in a small glass tube over mercury turns the glass distinctly violet in a single night; if moist the mercury becomes covered with a film of the red oxide, but if dry it appears to remain unattacked. A mixture of the emanation with oxygen produces carbon dioxide when passed through a lubricated stopcock.

### 3. Occurrence of Helium in the Gases Evolved from Radium Bromide.

The gas evolved from 20 milligrams of pure radium bromide (which we are informed had been prepared three months) by its solution in water and which consisted mainly of hydrogen and oxygen\* was tested for helium, the hydrogen and oxygen being removed by contact with a red-hot spiral of copper wire, partially oxidised, and the resulting water vapour by a tube of phosphorus pentoxide. The gas issued into a small vacuum-tube which showed the spectrum of carbon dioxide. The vacuum tube was in train with a small U-tube, and the latter was then cooled with liquid air. This much reduced the brilliancy of the  $\text{CO}_2$  spectrum, and the  $\text{D}_3$  line of helium appeared. The coincidence was confirmed by throwing the spectrum of helium into the spectroscope through the comparison prism, and shown to be at least within 0.5 of an Ångström unit.

The experiment was carefully repeated in apparatus constructed of previously unused glass with 30 milligrams of radium bromide, probably four or five months old, kindly lent us by Professor Rutherford. The gases evolved were passed through a cooled U-tube on their way to the vacuum-tube, which completely prevented the passage of carbon dioxide and the emanation. The spectrum of helium was obtained and practically all the lines were seen, including those at 6677, 5876, 5016,

\* Cf. Giesel, 'Ber.', 1903, 347.

4932, 4713, and 4472. There were also present three lines of approximate wave-lengths 6180, 5695, 5455, that have not yet been identified.

On two subsequent occasions the gases evolved from both solutions of radium bromide were mixed, after four days' accumulation which amounted to about 2.5 c.c. in each case, and were examined in a similar way. The  $D_3$  line of helium could not be detected. It may be well to state the composition found for the gases continuously generated by a solution of radium, for it seemed likely that the large excess of hydrogen over the composition required to form water, shown in the analysis given by Bodländer\* might be due to the greater solubility of the oxygen. In our analyses the gases were extracted with the pump, and the first gave 28.6, the second 29.2 per cent. of oxygen. The slight excess of hydrogen is doubtless due to the action of the oxygen on the grease of the stop-cocks, which has been already mentioned. The rate of production of these gases is about 0.5 c.c. per day for 50 milligrams of radium bromide, which is over twice as great as that found by Bodländer.

#### 4. *Production of Helium by the Radium Emanation.*

The maximum amount of the emanation obtained from 50 milligrams of radium bromide was conveyed by means of oxygen into a U-tube cooled in liquid air, and the latter was then extracted by the pump. It was then washed out with a little fresh oxygen which was again pumped off. The vacuum tube sealed on to the U-tube, after removing the liquid air showed no trace of helium. The spectrum was apparently a new one, probably that of the emanation, but this has not yet been completely examined, and we hope to publish further details shortly. After standing from the 17th to the 21st inst. the helium spectrum appeared, and the characteristic lines were observed identical in position with those of a helium tube thrown into the field of vision at the same time. On the 22nd the yellow, the green, the two blues and the violet were seen, and in addition the three new lines also present in the helium obtained from radium. A confirmatory experiment gave identical results.

We wish to express our indebtedness to the Research Fund of the Chemical Society for a part of the radium used in this investigation.

\* 'Ber.' (*loc. cit.*).

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"On the Intensely Penetrating Rays of Radium." By HON. R. J. STRUTT, Fellow of Trinity College, Cambridge. Communicated by LORD RAYLEIGH, F.R.S. Received August 5, 1903.

Radium is known to emit three types of radiation. These are—

(1) The  $\alpha$  rays, very easily absorbed by solids, and carrying a positive electric charge.

(2) The  $\beta$  rays, more penetrating than these, and negatively charged.

(3) The  $\gamma$  rays, intensely penetrating, and not conveying an electric charge at all.

In a paper published in the 'Phil. Trans.' for 1901, I investigated the relative ionisations of gases by the  $\alpha$  and  $\beta$  rays. The present communication may be regarded as a sequel to that one, and deals with the  $\gamma$  rays.

The radium employed was of activity 1000 (uranium = 1), and was contained in a glass cell, over which was cemented a piece of thin aluminium. The cell was placed in a cavity in a block of lead, and over it was placed a disc of lead 1 cm. in thickness. This it was considered would suffice to suppress all but the  $\gamma$  rays, which are much the most penetrating.

In measuring the electrical leakage, the electroscope method was employed. The apparatus was that described in a paper published in the 'Philosophical Magazine' for June, 1903, p. 681.

The radium, covered by the thick lead, was placed under the apparatus, and the rate of leak determined when the different gases filled the testing vessel.

The conditions were, of course, arranged so as to use a saturating E.M.F. The  $\gamma$  rays are so penetrating that there can be no question of their being appreciably absorbed in a moderate thickness of gas.

For the methods of preparation of the gases I must refer to the former paper.\*

The results were as follows; the rates of leak are given in scale divisions per hour, and are corrected to 30 inches pressure :—

\* 'Phil Trans.,' A, vol. 196, 1901, p. 508.

| Gas.                    | Rate of Leak.                                                             | Mean. |
|-------------------------|---------------------------------------------------------------------------|-------|
| Hydrogen .....          | 10.4, 10.5, 10.4, 11.2, 10.4, 11.2, 9.86, 10.1, 10.2.                     | 10.5  |
| Air .....               | 65.2, 66.6, 66.6, 60.0, 57.0, 61.5, 60.2, 63.0, 58.2,<br>58.3, 56.6, 56.2 | 62.1  |
| Oxygen .....            | 75.0, 74.2, 71.0, 74.1 .....                                              | 73.6  |
| Carbon dioxide .....    | 96.0, 95.4, 94.5, 95.1, 94.1, 94.7 .....                                  | 95.0  |
| Cyanogen .....          | 107, 104, 106, 106 .....                                                  | 106.0 |
| Sulphur dioxide .....   | 132, 126, 134, 135 .....                                                  | 132.0 |
| Chloroform .....        | 297, 298, 290, 327 .....                                                  | 303.0 |
| Methyl iodide .....     | 298, 292, 310, 291 .....                                                  | 298.0 |
| Carbon tetrachloride .. | 363, 351, 344, 349 .....                                                  | 352.0 |

The following table gives the relative ionisations, referred to air as unity. The values of the same constants for the  $\alpha$  and  $\beta$  rays formerly found are included, and also measurements of relative ionisation under Röntgen rays. These latter form part of an investigation not hitherto published.

#### Relative Ionisations.

| Gas.                     | Relative density. | Relative Ionisation. |               |                |               |
|--------------------------|-------------------|----------------------|---------------|----------------|---------------|
|                          |                   | $\alpha$ rays.       | $\beta$ rays. | $\gamma$ rays. | Röntgen rays. |
| Hydrogen .....           | 0.0693            | 0.226                | 0.157         | 0.169          | 0.114         |
| Air .....                | 1.00              | 1.00                 | 1.00          | 1.00           | 1.00          |
| Oxygen .....             | 1.11              | 1.16                 | 1.21          | 1.17           | 1.39          |
| Carbon dioxide .....     | 1.53              | 1.54                 | 1.57          | 1.53           | 1.60          |
| Cyanogen .....           | 1.86              | 1.94                 | 1.86          | 1.71           | 1.05          |
| Sulphur dioxide .....    | 2.19              | 2.04                 | 2.31          | 2.13           | 7.97          |
| Chloroform .....         | 4.32              | 4.44                 | 4.89          | 4.89           | 31.9          |
| Methyl iodide .....      | 5.05              | 3.51                 | 5.18          | 4.80           | 72.0          |
| Carbon tetrachloride.... | 5.31              | 5.34                 | 5.83          | 5.67           | 45.3          |

The determinations for the  $\gamma$  rays are less accurate than the former ones for the  $\alpha$  and  $\beta$  rays, on account of the very much smaller rates of leak which have to be measured. I think, if this be taken into account, there is no reason to doubt that, within the limits of experimental error, the  $\gamma$  rays give the same values as the  $\beta$  rays. These values are nearly proportional to the density of the gas, except in the case of hydrogen. The law which holds in the case of Röntgen rays is totally different.

This conclusion throws some light on the nature of the  $\gamma$  rays. The view seems to be gaining ground that these are Röntgen rays, produced by the impact of the  $\beta$  rays on the radium itself.\* This theory seems

\* See, for instance, Madame Curie, 'Thèses présentées à la Faculté des Sciences,' 1903, p. 83.



to have much to recommend it. The  $\beta$  rays should, by analogy with the cathode rays in a vacuum tube, produce Röntgen rays when they strike a solid obstacle, and these Röntgen rays should be much more penetrating than the  $\beta$  rays themselves. The  $\gamma$  rays seem at first sight to be just what should be expected. But the present paper shows that in one respect, at all events, the  $\gamma$  rays behave quite differently to Röntgen rays, while, on the other hand, they resemble the  $\alpha$  and  $\beta$  rays. There seems to be a possibility that they too are of a corpuscular nature, though uncharged with electricity. This would account for the absence of magnetic deflection

I do not think that the absence of conspicuous Röntgen radiation is very hard to understand, if we consider that the current emitted in cathode rays by a square inch of intensely active radium is only  $10^{-11}$  ampères; the current through a focus tube is of the order  $10^{-2}$  ampères, and probably a great part of this is carried by the cathode rays.

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"On the Formation of Definite Figures by the Deposition of Dust." By J. AITKEN, F.R.S. Received July 13, 1903.

(Abstract.)

The author discusses the experiments in Dr. W. J. Russell's paper,\* finding from optical examination of the phenomena that the dust falls out from the layer of air creeping along the lower side of the plate, and this dust-free layer of air turns round the edges of the plate and flows over and in contact with its upper surface, so protecting it from any deposit of dust where the current has sufficient horizontal motion; but deposition takes place where the motion is checked by the currents meeting, or where obstructions cause eddies and break the stream-lines, or by anything that tends to prevent the dustless layer of air flowing over the upper surface of the plate.

"Mean Results of Monthly Determinations of the Magnetic Elements at the Valencia Observatory, Cahirciveen., lat.  $51^{\circ} 56' N.$ , long.  $10^{\circ} 15' W.$ " By J. E. CULLUM. Received June 5, 1903.

Absolute Declination, 1902.

| Date.           | G.M.T.      | Declination.            | Inclination.<br>Mean of two<br>needles. |
|-----------------|-------------|-------------------------|-----------------------------------------|
| January .....   | 10. 10 A.M. | $21^{\circ} 26' 3'' W.$ | $68^{\circ} 25' 1''$                    |
| February .....  | 10. 2       | 26.2                    | 24.1                                    |
| March .....     | 10. 4       | 25.7                    | 24.9                                    |
| April ... ..    | 9. 55       | 23.8                    | 25.2                                    |
| May .....       | 10. 7       | 23.1                    | 24.8                                    |
| June .....      | 9. 57       | 25.5                    | 24.4                                    |
| July .....      | 10. 5       | 25.3                    | 23.6                                    |
| August .....    | 9. 52       | 21.5                    | 23.4                                    |
| September ..... | 9. 53       | 24.8                    | 23.1                                    |
| October .....   | 10. 0       | 21.7                    | 22.9                                    |
| November .....  | 10. 2       | 22.9                    | 23.1                                    |
| December .....  | 10. 9       | 23.7                    | 22.2                                    |
| Means .....     | 10.1 A.M.   | $21^{\circ} 24' 2''$    | $68^{\circ} 23' 9''$                    |

\* 'Roy. Soc. Proc.,' vol. 71, p. 285.

## Force Observations, 1902 (C.M.G.).

| Date.           | H.F.    | V.F.<br>(H.F. tan dip.) | T.F.<br>(H.F. sec dip.) |
|-----------------|---------|-------------------------|-------------------------|
| January .....   | 0·17822 | 0·45056                 | 0·48453                 |
| February .....  | 0·17840 | 0·45043                 | 0·48465                 |
| March .....     | 0·17822 | 0·45050                 | 0·48445                 |
| April .....     | 0·17817 | 0·45047                 | 0·48442                 |
| May .....       | 0·17850 | 0·45115                 | 0·48518                 |
| June .....      | 0·17838 | 0·45068                 | 0·48470                 |
| July .....      | 0·17831 | 0·45020                 | 0·48423                 |
| August .....    | 0·17825 | 0·45002                 | 0·48399                 |
| September ..... | 0·17825 | 0·44986                 | 0·48389                 |
| October .....   | 0·17824 | 0·44977                 | 0·48379                 |
| November .....  | 0·17843 | 0·45032                 | 0·48438                 |
| December .....  | 0·17853 | 0·45022                 | 0·48433                 |
| Means .....     | 0·17833 | 0·45035                 | 0·48438                 |

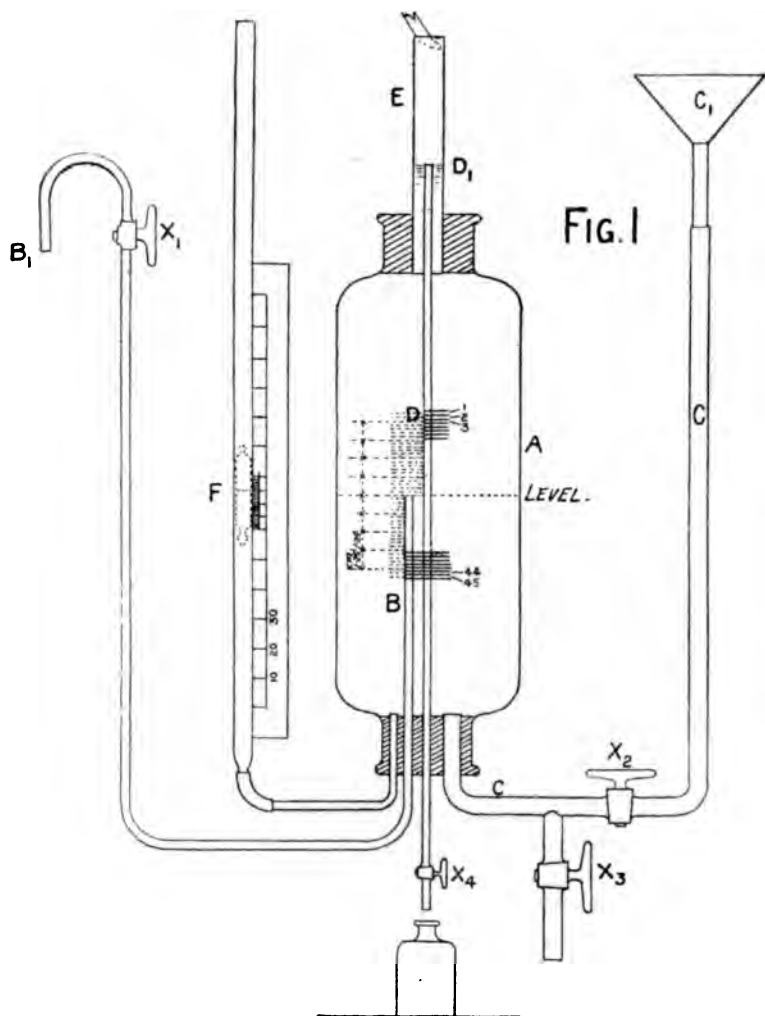
[These annual reports will in future be published, along with the other British magnetic observations, in the Reports of the National Physical Laboratory. The Falmouth magnetic observations are published in the Annual Reports of the Royal Cornwall Polytechnic Society, and will also be reprinted in the Reports of the National Physical Laboratory.—SEC.]

“On the Measurement of the Diffusion of Salts in Solution.” By J. C. GRAHAM. Communicated by Professor W. E. AYRTON, F.R.S. Received May 14,—Read June 11,—Received in revised form June 25, 1903.

In order to get the solution of the salt below the pure water which is above it, without any intermixing at their common surface, the apparatus was used which is shown in fig. 1. A is a cylindrical glass vessel containing a solution of the salt to be investigated, in the lower half, and containing pure water in the upper half. The internal diameter of the vessel was about 125 mm., and the depth of the cylindrical part about 300 mm. B is a tube which passes up through the bottom of the vessel, and is continued outside in the manner shown. C is a tube which opens into the lowest part of the vessel and is connected with a funnel  $C_1$ . D is a small tube which passes up the centre of the vessel to the point  $D_1$ .

The vessel is first completely filled with pure water through the funnel  $C_1$ , until it has risen to the point marked  $D_1$ ; the cocks  $X_3$  and  $X_4$  being closed, and the cocks  $X_1$  and  $X_2$  open.

The vessel is then ready for the introduction of the salt solution, which is allowed to drop into the funnel  $C_1$  from which it passes through the pipe  $C$  into the vessel  $A$ , where it gradually floats the water upwards and continually forces it out through the pipe  $B$ .



It will be noticed that the water which is thus forced out is that which lay below the point marked "level"; after say an hour the first portions of the salt solution reach the point marked "level" and are then forced out, and ultimately the salt solution of the normal density, *i.e.*, the density used, occupies the lower half of the vessel, and pure water occupies the upper half, and there is no mixing at the common surface.



C<sub>1</sub>, the top stratum passes down through the tube D and is reserved for weighing. In the same manner all the remaining strata are drawn off.

The specific gravity of each stratum is ascertained.

These specific gravities when plotted give a curve from which  $\kappa$  can be calculated.

Fig. 2 shows how this was done with a solution of chloride of sodium of density 1026.892. The contents of the 25 c.c. sp.g. bottle weighed 25.6723 grammes. I assumed (which is not quite correct) that the weight of salt was 0.6723 gramme, and plotted this as 300 mm.

In the same way the weights of salt in 25 c.c. of all the other strata were plotted. The small circles show the curve so obtained. And from this curve  $\kappa$  can be calculated by means of Fourier's equation

$$u = \frac{1}{2} + \frac{1}{\sqrt{\pi}} \left\{ \frac{x}{2\sqrt{\kappa t}} - \frac{1}{3} \left( \frac{x}{2\sqrt{\kappa t}} \right)^3 + \frac{1}{5} \cdot \frac{1}{2} \left( \frac{x}{2\sqrt{\kappa t}} \right)^5 - \text{etc.} \right\}.$$

In this particular case diffusion went on for 111½ hours and the average value of  $\kappa t$  for 111½ hours was 3.95, therefore  $\kappa$  (for one hour) = 3.95/111½ = 0.0355.

This equation gives a curve which is symmetrical with respect to the line AB. The small crosses were obtained by marking the small circles on tracing paper and turning the tracing paper through 180° round the point O. The near agreement of the two curves is a good test of the accuracy of the observations.

The fluids and the room where the experiment was made were at about 14° C, but it was not possible to keep the temperature of the room constant. The vessel A was very completely enclosed in flannel.

The labour of calculating  $\kappa t$  from any observed curve is obviated by means of the curves shown on fig. 3. Here the values of  $u$  at the distances 1.25, 2.5, 3.75, and 5 cm. were calculated from the above equation, for successive values of  $\kappa t$  from 1 to 10, and plotted to the scale of 300 mm. = unity. For example, the figure 98.45 (the average of 98.2 and 98.7 see fig. 2) where  $x = 1.25$  cm. is seen by the curve to give the value 3.93 for  $\kappa t$ . Inasmuch as these calculations of  $u$  are very laborious, I have given the values in the following table. Each must be multiplied by 300 if 300 mm. is taken as unity. With such curves the value of  $\kappa t$  is obtained by inspection.

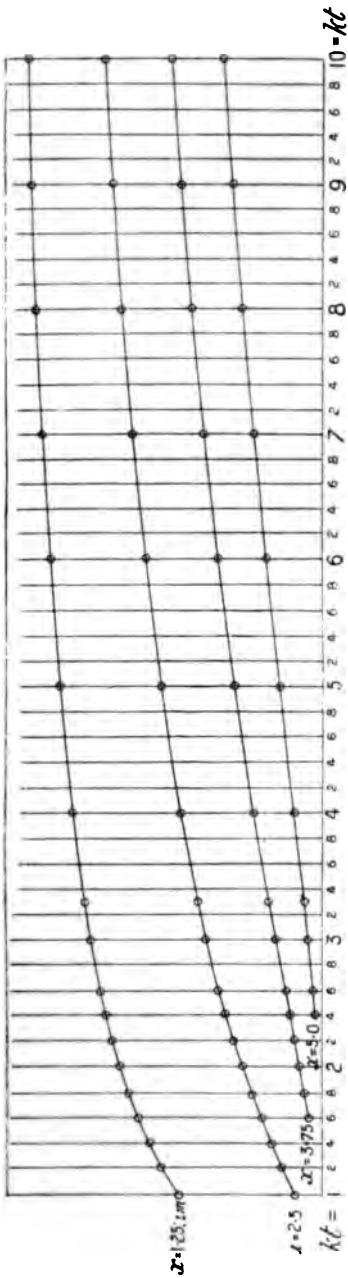


FIG. 3.

(This drawing is to a reduced scale.)

| $\kappa t =$   | 1.    | 1.2.  | 1.4.  | 1.6.  | 1.8.  | 2.    | 2.2.  | 2.4.  | 2.6.  |
|----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| $x = 1.25$ cm. | .1884 | .2098 | .2276 | .2424 | .255  | .266  | .2756 | .2841 | .2918 |
| $x = 2.5$ cm.  | .0386 | .0532 | .0676 | .0812 | .0939 | .1056 | .1171 | .1268 | .1365 |
| $x = 3.75$ cm. | ..    | ..    | ..    | .018  | .0241 | .0303 | .0369 | .0435 | .05   |
| $x = 5.0$ cm.  | ..    | ..    | ..    | ..    | ..    | ..    | ..    | .0109 | .0143 |

| $\kappa t =$   | 3.    | 3.3.  | 4.    | 5.    | 6.    | 7.    | 8.    | 9.    | 10.   |
|----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| $x = 1.25$ cm. | .3049 | .3133 | .3203 | .3463 | .3591 | .3692 | .3773 | .3842 | .3892 |
| $x = 2.5$ cm.  | .1538 | .1652 | .1879 | .2146 | .2352 | .252  | .2659 | .2778 | .287  |
| $x = 3.75$ cm. | .0623 | .0721 | .0923 | .1177 | .1395 | .158  | .1743 | .1884 | .2009 |
| $x = 5.0$ cm.  | .0205 | .025  | .0395 | .0569 | .074  | .0913 | .1056 | .1193 | .1318 |



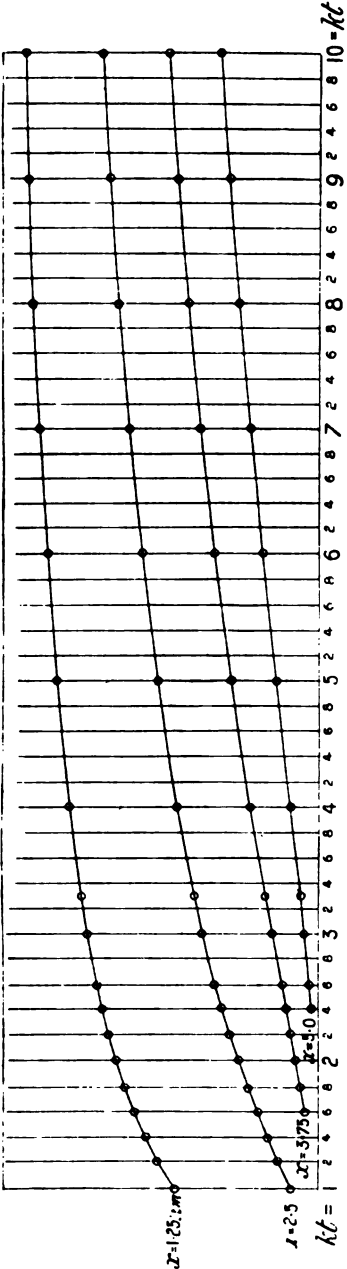


FIG. 3.  
(This drawing is to a reduced scale.)

| $\kappa t =$           | 1.    | 1.2.  | 1.4.  | 1.6.  | 1.8.  | 2.    | 2.2.    | 2.4.  | 2.6.  |
|------------------------|-------|-------|-------|-------|-------|-------|---------|-------|-------|
| $x = 1.25 \text{ cm.}$ | ·1884 | ·2098 | ·2276 | ·2424 | ·255  | ·266  | ·27 5 6 | ·2841 | ·2918 |
| $x = 2.5 \text{ cm.}$  | ·0386 | ·0532 | ·0676 | ·0812 | ·0939 | ·1056 | ·1171   | ·1268 | ·1365 |
| $x = 3.75 \text{ cm.}$ | ..    | ..    | ..    | ·018  | ·0241 | ·0303 | ·0369   | ·0435 | ·05   |
| $x = 5.0 \text{ cm.}$  | ..    | ..    | ..    | ..    | ..    | ..    | ..      | ·0109 | ·0143 |

| $\kappa t =$           | 3.    | 3.3.  | 4.    | 5.    | 6.    | 7.    | 8.    | 9.    | 10.   |
|------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| $x = 1.25 \text{ cm.}$ | ·3049 | ·3133 | ·3203 | ·3463 | ·3591 | ·3692 | ·3773 | ·3842 | ·3892 |
| $x = 2.5 \text{ cm.}$  | ·1538 | ·1652 | ·1879 | ·2146 | ·2352 | ·252  | ·2659 | ·2778 | ·287  |
| $x = 3.75 \text{ cm.}$ | ·0623 | ·0721 | ·0923 | ·1177 | ·1395 | ·158  | ·1743 | ·1884 | ·2009 |
| $x = 5.0 \text{ cm.}$  | ·0205 | ·025  | ·0395 | ·0569 | ·074  | ·0913 | ·1056 | ·1193 | ·1318 |

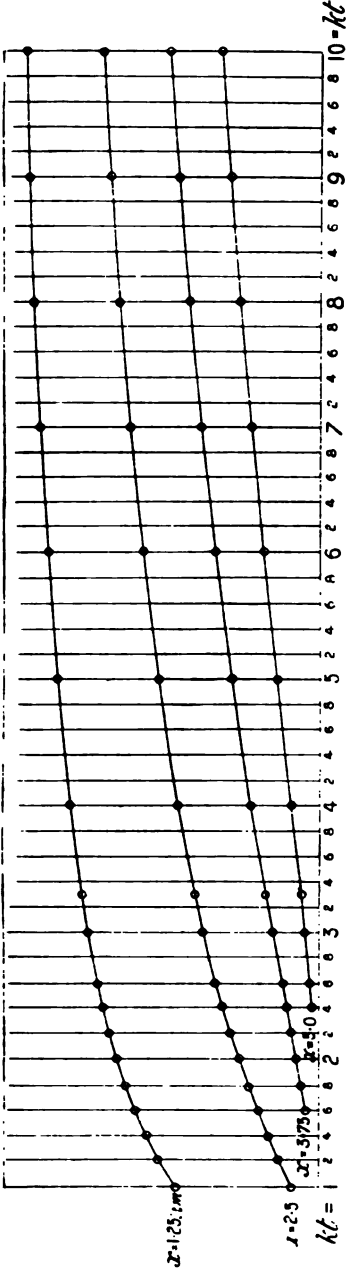


Fig. 3.  
(This drawing is to a reduced scale.)

| $\kappa t =$   | 1.    | 1.2.  | 1.4.  | 1.6.  | 1.8.  | 2.    | 2.2.  | 2.4.  | 2.6.  |
|----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| $x = 1.25$ cm. | .1884 | .2098 | .2276 | .2424 | .255  | .266  | .2756 | .2841 | .2918 |
| $x = 2.5$ cm.  | .0386 | .0532 | .0676 | .0812 | .0939 | .1056 | .1171 | .1268 | .1365 |
| $x = 3.75$ cm. | ..    | ..    | ..    | .018  | .0241 | .0303 | .0369 | .0435 | .05   |
| $x = 5.0$ cm.  | ..    | ..    | ..    | ..    | ..    | ..    | ..    | .0109 | .0143 |

| $\kappa t =$   | 3.    | 3.3.  | 4.    | 5.    | 6.    | 7.    | 8.    | 9.    | 10.   |
|----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| $x = 1.25$ cm. | .3049 | .3133 | .3293 | .3463 | .3591 | .3692 | .3773 | .3842 | .3892 |
| $x = 2.5$ cm.  | .1538 | .1652 | .1879 | .2146 | .2352 | .252  | .2659 | .2778 | .287  |
| $x = 3.75$ cm. | .0623 | .0721 | .0923 | .1177 | .1395 | .158  | .1743 | .1884 | .2009 |
| $x = 5.0$ cm.  | .0205 | .025  | .0395 | .0569 | .074  | .0913 | .1056 | .1193 | .1318 |

"Surface Flow in Crystalline Solids under Mechanical Disturbance." By G. T. BEILBY. Communicated by F. H. NEVILLE, F.R.S. Received in revised form May 23,—Read June 18, 1903.

[PLATES 9 and 10.]

In a paper read before the British Association at Glasgow, in 1901, and in a further paper communicated to the Royal Society in February, 1902, I described certain observations on the surface structure of metals and other solids. These observations went to show that the effect of mechanical treatment of metals by cutting tools or by polishing agents is to produce a surface layer or film whose structure and appearance are distinct from those of the undisturbed substance below. This surface layer has no appearance of crystalline structure, but it has a certain structure granular or scale-like, which lends itself to the formation of smooth, rounded, or flowing forms like those assumed by a viscous liquid. It was also observed that the edges of a piece of ductile metal which has been torn asunder, generally, if not invariably, present the same appearance of viscous flow and of granular or scale-like structure.

Mr. F. H. Neville having suggested that the appearance of granular or spicular structure which is seen by oblique illumination might be due to the presence on the metal surface of crystalline facets so minute as to be themselves invisible but capable of producing spots of light like fixed stars seen through a telescope, the apparent size of the spots being solely determined by the aperture of the object glass, I arranged to make a fresh series of observations, using an oil immersion lens of the highest numerical aperture and illumination by normally reflected rays.

The result of these observations has been that under the more exacting conditions, the general appearance of the surface suggests, as strongly as ever, the flow of a viscous, semi-solid substance, while nothing of the nature of crystalline facets has been detected.

In speculum metal it was first noticed that the stages in the flow of the surface layer during polishing could be definitely traced as it spread over and across the ridges and furrows of the crystalline metal below; figs. 9, 10, 11, 12 show the formation of the surface layer and its removal by solution. Speculum metal being an alloy, it was felt that in this case the effects of flow might to some extent depend on the presence of the eutectic in which the crystalline grains are embedded. In order, therefore, to eliminate this possible complication the same observations were repeated using a piece of pure crystalline antimony. In this also the appearances of flow were unmistakable, being even more marked than in speculum metal.

The experiment was made by filing a flat surface on the antimony with a very fine watchmaker's file. Even with this smooth file the surface of the antimony was a good deal broken into crystalline ridges and hollows by the splintering of the brittle metal. After as flat a face had been obtained as was possible with this tool, it was rubbed, still in the direction of the file marks, on the finest emery paper (No. 00 French) till the file marks had disappeared, only the deeper pits and hollows remaining. Fig. 2 shows the surface at this stage, from which it is seen that the general character of the ridges and furrows left by the emery is smooth and rounded and that the smaller pits, which had resulted from the breaking out of crystalline chips, are in many cases losing their angularity and assuming a rounded form. The specimen was next rubbed across the line of the emery scratches on a polishing block covered with washleather sprinkled with the finest rouge. Fig. 3 shows the surface at this stage. The polishing has spread the metal across the ridges left by the emery like a viscous paste, sometimes filling the furrows and sometimes bridging them over. In some cases the line of the furrow can only be traced by the row of holes in the covering film. The circular form and the smooth rounded edges of the holes are quite consistent with the other appearances of viscous flow.

A part of the surface was now etched with a solution of potassium cyanide. Fig. 4 shows the effect of the solvent in removing the layer which has been spread over the surface by the polishing. The portion of the original photograph, which is reproduced here, shows on the left side the effect of the removal of the surface, and on the right a portion which was protected from the action of the solvent by varnish. The removal of the surface layer has again uncovered the furrows and ridges left by the emery, and the impression conveyed by the preceding photograph (fig. 3) is confirmed, namely, that the ridges and furrows had been covered over, not levelled down or removed. It is further seen that the understructure of the ridges is rough and crystalline, the appearance of the flow given by the polishing having been only skin deep.

In examining the specimen under the microscope the attention was arrested by the curious appearance presented by two of the pits on the surface, which appeared as if covered over with a film of greatly diminished reflecting power as compared with the rest of the surface. A search over other parts of the surface disclosed a number of similar pits which showed the covering film with greater distinctness. A group of these pits is shown on fig. 5; in these the solvent has acted on the film less than it has on the covering of the pit seen in fig. 4, and the continuation of the surface markings can be traced across the film over the pit.

On another part of the surface which had not been exposed to the

solvent a pit was discovered in which the film appeared to be in process of building up, fig. 6. It is difficult to believe that the flowing metal could be carried across the pit from side to side without the help of some support from below. It seems most probable that this support has been provided by small granules or flakes scraped off at an earlier stage, which had lodged in the pit filling it loosely up to the general surface level. Granules or flakes have been noticed in polishing speculum metal, and their lodgment in the deeper scratches on the surface has been actually observed. Fig. 7 shows a surface across which a very fine scratch with a needle has been made. On polishing with emery across the line of the scratch the shavings of metal were caught and heaped up in the deep furrow made by the point of the needle.

These observations on the polishing of antimony show plainly that under certain conditions this brittle, crystalline metal can be spread over an irregular surface so as to form a smooth varnish-like covering by which all the asperities are smoothed and rounded into gently-flowing curves. It is further seen that this surface layer or film when, as in the pits of figs. 5 and 6, it is not in solid contact with the more massive metal underneath, has a much diminished reflecting power. This illustrates in a new way the fact which I have referred to in my earlier papers, that metal films as they become reduced in thickness show a diminished reflecting power, a corresponding increase of transparency at the same time taking place.

The pressure necessary to produce surface flow in antimony is very slight. The specimen was rubbed back and forwards on the leather-faced block by the pressure of the fore-finger. The seizing of the metal surface by the rouged leather could be distinctly felt as the specimen was passed over it, and was obviously more marked with rouged than with unrouged leather. On a moderately flat surface the seizing seems to take place uniformly all over the surface and not merely at a few points at a time, so that each passage over the leather changes the whole surface slightly.

When glass is furrowed by fine emery and then polished across the furrows appearances of flow similar to those seen in metals can be detected. I have not yet succeeded in making photographs which show this in a satisfactory way, but hope to do so soon.

The extremely slight mechanical treatment which will suffice to cause molecular movement and flow on the surface of a highly crystalline substance is seen in a remarkable way in the behaviour of calc-spar.

A crystal of Iceland spar was split so as to present a fresh smooth face which had never been touched or rubbed in any way. A small drop of very dilute hydrochloric acid (containing about 0.2 per cent. HCl) was placed on this fresh face and after 10 to 15 seconds was removed by touching the spot with a torn edge of soft filter paper.

The liquid tends to spread over the face in all directions, no doubt owing to the perfect freedom from dust and grease of the surface; but, as far as possible, it is desirable to confine the etching action to one spot so that a comparison between the etched and unetched portions may be more readily made. Slight etching resulted from the treatment, but the etched surface, though slightly undulating and irregular, showed no new structure or markings. When the experiment is repeated a number of times it is generally found that the surface, though slightly lowered where the acid has acted, is otherwise unaltered. The face of the crystal was now firmly stroked a few times in one direction with the point of the fore-finger covered with clean soft wash-leather. Under the microscope the surface was still smooth and unmarked by the stroking. A drop of the dilute acid was placed on a part of the stroked face which had not been touched by the previous application of acid. The drop flattened to a hemisphere but did not spread. After 10 to 15 seconds it was removed as before. The pit produced had well-defined edges and the flat bottom was covered with furrows and ridges running in the direction of the strokes with the finger.



This experiment was repeated in a variety of ways and on all of the three parallel sets of faces. The direction of the strokes was varied so as to make a number of different angles with the cleavages. In every case the result was the same, *even a single stroke showed unmistakably on the etched surface.*

Plate 9, fig. 1, shows a part of the etched surface. The unetched portion has the smooth glass-like surface of the natural face, only a few very faint scratches being visible under the most searching examination. Faint cleavage lines crossing the face indicate that the stroking had not been parallel with any of the natural cleavages.

The number and depth of the flow lines is influenced by the amount of the stroking and by the pressure exerted by the finger. Flow lines were distinctly developed by a single firm stroke in which, it was roughly estimated, the pressure exerted did not exceed 4 lbs. per square inch. In this case the flow lines were obviously fewer than they were when a number of strokes had been given.

Some indication of the depth to which the molecular disturbance has penetrated is given by the additional time required for the acid to dissolve and remove all traces of the disturbance. If the acid is left on the surface for a sufficiently long time, for instance, with the acid in question, for 30 to 60 seconds, no trace of the flow lines remains, and



the etched surface presents the same appearance as the etched surface of an untouched face, the limits of the disturbance have been reached. The depth to which the disturbance penetrates is not much affected by continued stroking. The influence of the stroking is therefore limited to a very thin surface film, but within this limit it is quite unmistakable. If a stroked and etched surface is further stroked its details become rounded and glazed over.

The nature of the structural change which has taken place in the surface layer of the Iceland spar as it is disclosed by etching will be referred to in another connection. For the present it is proposed simply to discuss these observations in their immediate bearing on the surface flow of crystalline solids. The most striking facts brought to light by this experiment are; that a solid structure can be profoundly modified below its surface while the surface itself appears intact; and further, that this change can be brought about by so gentle an agent as the softly covered finger.

There appear to be two directions in which the explanation of the first fact may be sought; either there has been a transmission of stress from the surface which has produced a state of strain along the lines followed by the moving points of the polishing material; or there has been a movement of translation of the molecules resulting in flow of the substance similar to that which is seen at the surface of crystalline metals.

The first of these suggestions finds very little support from the facts of the case. The flow lines are equally deep and distinct whether they run parallel to or at an angle with the cleavages. If the flow lines exist in the stroked but unetched surface as hidden clefts it might reasonably be expected that the chief effect of the stroking would be felt along the natural cleavages; but this is not the case. Again, the prompt and uniform action of the solvent in first removing the *whole* of the uppermost layer of the surface, suggests that this covering film is fairly homogeneous and that it is not a kind of mosaic with concealed joints. This remark applies also to the kind of under-structure disclosed by the removal of the surface; the rounded details of the ridges and furrows do not in the least suggest the clean sharp planes and angles of cleavages.

It seems, on the whole, most probable that the surface molecules are set in gliding motion by the moving leather, so that they form an extremely thin film of fluid among which the larger particles or aggregates are dragged, causing the furrows which are afterwards disclosed by etching. The film of gliding molecules will be subject to surface tension, which would account for the perfectly smooth surface which is left by polishing. The fluid film when left to itself would naturally close over the asperities like an unbroken skin, thus covering up all trace of the disturbance caused by the stroking.

The experiments with antimony show the same phenomena in a much rougher way, and in that case we gain a slight clue to the mechanism by which the flow is produced. Beginning at the rougher end of the polishing process, we can see that the projecting points of the file plough their way through the metal carrying with them a certain proportion of it, but also leaving behind in the furrows and on the ridges a smooth covering film of metal, which has flowed at the moment when the moving point with its burden of accumulated metal passed over it. With the emery grains the same operation is repeated, but in their case there is less ploughing action, and the proportion of the metal which adheres to the polishing agent is much greater and the flowing action is more pronounced. When the rouge stage is reached there appears to be no cutting or ploughing action to speak of, the particles of rouge seem to have the power of seizing the surface so as to set the molecules gliding without actually removing much metal. As the molecules or molecular aggregates glide over each other within the range of their molecular forces, the conditions of the liquid state are to a considerable extent fulfilled and the forms assumed by the surface are determined, as in a viscous liquid, by surface tension. This view will be more fully discussed in connection with observations on "The Effect of Heat on Thin Films and Surface Layers" and on "The Aggregation of Solids under the Influence of the Molecular Forces" which will be detailed in Parts II and III of this paper. Whether the minute elements which are made to glide over each other in a state of comparative freedom are individual molecules, or whether they are aggregates of molecules is still an open question; but numerous observations have been collected which may throw light on the matter. These it is proposed to present in Part IV of this paper on "Granular and Spicular Structure and the Transparence of Metals."

In a previous communication, various experiments were described which showed that glass and other silicates in a finely divided state can be welded together into larger masses by pressure. In this way a mass of thin films of blown glass was pressed into a compact layer. In grinding glass in an agate mortar it was found that the rolling under the pestle tended to aggregate the finer particles into granular masses.

In recent experiments with calc-spar it has been found that the appearance of surface flow can be produced by pressure. One of the faces of a crystal of Iceland spar was rubbed, first on a fine file and then on the emery block till a fine grained surface was produced. By strongly pressing the roughened face on a smooth, hard, slightly convex surface, little patches of flow were developed. These patches were perfectly distinct from the roughened surface by which they were surrounded, and their boundaries were well defined and flowing like those of a drop of liquid pressed between two plates of glass. The surface of these patches had the perfect smoothness of a liquid surface. 4

A thin field of magnesium oxide was obtained by holding a glass slip over burning magnesium. Films of any degree of thickness may be readily obtained in this way. The film selected was translucent, and was bluish-white by reflected light. The rounded end of an agate pestle was lightly pressed on the film and slightly rolled upon it. As the film adhered more and more firmly to the glass, the pressure was increased. The experiment is not always successful, as the film of oxide sometimes sticks to the pestle instead of to the glass, but with a little care it is easy to obtain flowed or welded patches of magnesium oxide. These patches are smooth and transparent, like glass; their structure will be referred to again in another connection.

In beating or planishing metal on a smooth surface, the flow is not so strictly confined to the surface nor to the exact spot at which the pressure is applied, as it is in the case of hard, brittle substances. In the softer metals the flow proceeds much further from the centre of pressure than it does in the harder. Very minute crystalline fragments of antimony or bismuth can be beaten into scales, and their flow appears to be as perfect as that of gold or silver. As the size of the particles is increased, the outer edge of the minute plates develops notches and radial cracks, showing that the limits of flow have been exceeded.

It appears not unlikely that an accurate method of comparing the hardness and malleability of metals might be based on the behaviour of minute particles during their flow under uniform conditions of pressure.

#### DESCRIPTION OF PLATES 9 AND 10.

##### PLATE 9.

Fig. 1.—*Iceland spar* showing etched and unetched surface.

Light, transmitted slightly oblique, green screen.

Objective 16 mm. Apochromat. N.A. 0.3.  $\times 215$ .

Fig. 2.—Crystalline antimony after rubbing on fine emery paper.

Light, normal reflected, green screen.

Objective 3 mm. Oil immersion. Apochromat. N.A. 1.4.  $\times 775$ .

Fig. 3.—The same after polishing on rouged leather.

Light and objective as in fig. 2.  $\times 775$ .

Fig. 4.—The same after partial etching with KCy.

Light and objective as in fig. 2.  $\times 775$ .

Fig. 5.—The same showing pits covered with film of flowed metal.

Light and objective as in fig. 2.  $\times 775$ .

Fig. 6.—The same showing another pit over which a film is being built up by the flowing metal.

Light and objective as in fig. 2.  $\times 775$ .

All of the above are from direct photographs without enlargement or reduction.

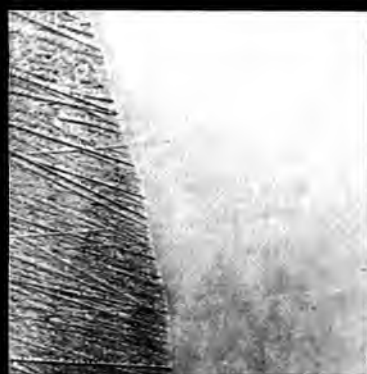


Fig. 1. X 215



Fig. 2. X 775

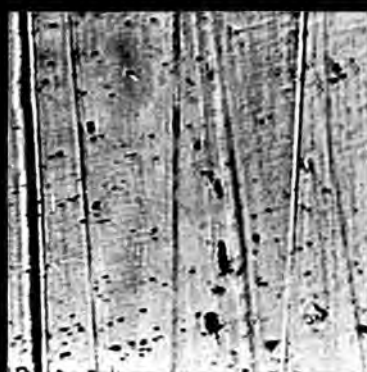


Fig. 3. X 775



Fig. 4. X 775



Fig. 5. X 775



Fig. 6. X 775





Fig. 7. X 1500

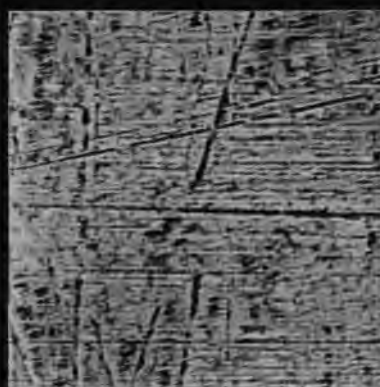


Fig. 8. X 775



Fig. 9. X 775



Fig. 10. X 775

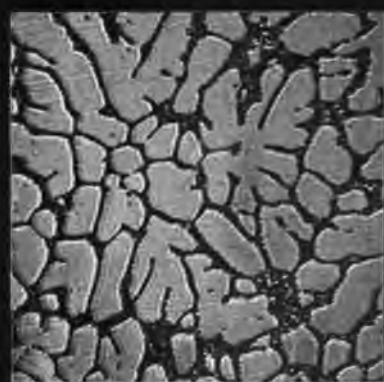


Fig. 11. X 775

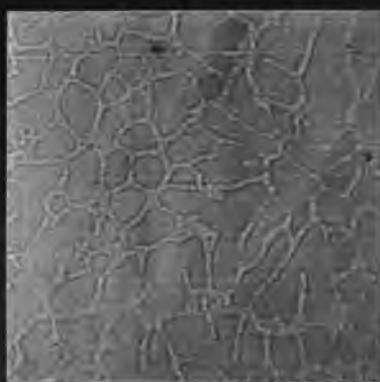


Fig. 12. X 775



## PLATE 10.

Fig. 7.—*Speculum metal*, the broad horizontal band is a very fine needle scratch in which the particles of metal from the emery scratches have been intercepted.

Light, normal reflected, green screen.

Objective 3 mm. Oil immersion. Apochromat. N.A. 1.4.  $\times 1500$ .

Fig. 8.—*Tool steel hardened and tempered* showing flow of the metal during emery grinding.

Light and objective as in fig 7.  $\times 775$ .

Fig. 9.—*Speculum metal* polished on rouged leather across the furrows left by fine emery, showing flow of metal across the furrows.

Light and objective as in fig. 7.  $\times 775$ .

Fig. 10.—*The same* further polished. The outlines of the crystalline grains show under the surface.

Light and objective as in fig. 7.  $\times 775$ .

Fig. 11.—*The same* with the surface film removed by KCy showing the grains surrounded by the eutectic.

Light and objective as in fig. 7.  $\times 775$ .

Fig. 12.—*The same* again polished on rouged leather, showing the formation of a fresh film on the surface.

Light and objective as in fig. 7.  $\times 775$ .

All of the above are from direct photographs without enlargement or reduction.

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"The Effects of Heat and of Solvents on Thin Films of Metal."

By G. T. BEILBY. Communicated by F. H. NEVILLE, F.R.S.

Received June 4,—Read June 18, 1903.

[PLATES 11—13.]

In the Bakerian Lecture of 1857,\* on "Experimental Relations of Gold and other Metals to Light," Faraday described a series of experiments which were designed to throw light on the structure and behaviour of metals in their most attenuated forms. Probably the most remarkable of these experiments were those in which leaves and films of gold and silver supported on glass were changed by a temperature much below the melting point of the metal from a moderate translucence to clear transparency and from high metallic reflecting power to comparative deadness.

These remarkable experiments seem practically to have dropped out of sight during the past 45 years for, so far, I have found no reference to this particular phenomenon in the papers of more recent workers on the reflecting and absorbing powers of thin metal films, and many physicists to whom I have shown these Faraday films have received them as a novelty.

The significance and explanation of the change produced by heat is discussed by Faraday at several stages of the lecture. Two alternative explanations are suggested by him. Under the first, it is supposed that the heating may act by gathering the metal into small aggregates, thus leaving the surface like a grating through which light can freely pass. Under the second, the leaf or film is supposed to be made up of scale-like films, the effect of heating being to open these up like the louvres of a blind, thereby allowing the light to pass freely between them. A third suggestion may be read into some of Faraday's remarks, namely, that metal in the non-reflecting transparent condition is an allotropic modification of the common or reflecting form.

While studying the appearance and structure of surface films on metals in their more massive forms,† it occurred to me that considerable light might be thrown on that subject by a parallel study of the behaviour of translucent films supported on glass, as these present the great advantage for microscopical examination that they permit of the use of transmitted light.

The result of this parallel study has been to show that both aggregation and film formation come into play when metal leaves and films are heated, but that an intrinsic transparency exists altogether apart from these phenomena.

\* 'Phil. Trans.,' 1857, p. 145.

† 'British Association Report,' 1901, p. 604.

As a further result of this study, it is now suggested that the behaviour of surface films during heating may be most satisfactorily explained on the hypothesis that even at a temperature much below the melting point, sufficient freedom is conferred on the molecules by the heating to enable them to behave as the molecules of the liquid metal would do, and to arrange themselves under the influence of surface tension either in films or in drop-like or granular forms.

Faraday definitely associated diminished transparence and enhanced reflecting power with a state of strain induced by pressure and burnishing. My later observations confirm and extend this conclusion and show that, contrary to my first impression, all mechanical disturbance of the surface by polishing or burnishing tends to diminish transparence and to increase the reflecting power.

In gold an olive green colour by transmitted light is generally associated with the strained condition, while a great variety of shades of colour, ranging from ruby-red to violet, are found in the annealed metal.

A gold leaf, after annealing on glass, retains all the ribs and markings of the original leaf. These interfere with the uniform adhesion between the metal and the glass, and lead to obvious breaks in continuity. Fig. 13 (Plate 11) shows a piece of gold leaf annealed on glass. Small granular aggregations are seen, but the continuity of the film between these is not so obvious.

Faraday describes how he prepared gold films of varying thickness and of great smoothness and continuity by placing specks of phosphorus on the surface of a dilute solution of gold chloride.

Films made in this way were annealed by heating on glass. Figs. 15 to 18 show the effects of annealing on films of various degrees of thickness.

Before annealing, the thicker films (figs. 15, 16, 17) were olive-green by transmitted light and had a full yellow colour and metallic reflection by reflected light. The thickest film, fig. 15, required a very intense light to show its green translucence. Fig. 16 had the same depth of colour as gold leaf, and fig. 17 was thinner and paler. Fig. 18 was much thinner than any of the others, showed hardly any metallic reflection and its colour was blue-purple by transmitted light.

After annealing the colour of this film was rose-pink by transmitted light. The photograph shows that it was quite continuous, but with thickenings or aggregations distributed regularly over the surface. The photograph has been made somewhat dark in order that the structure may be shown more distinctly, but as seen under the microscope the surface was entirely free from dark or opaque patches.

In fig. 17 the retraction into globular or rounded forms of greater opacity is very pronounced, but the continuous transparent film

covering the whole surface is distinctly seen. Under the microscope this film was of a very pale pink colour, the thicker parts being of a slightly deeper shade. The opaque-looking granules of the photograph were really of a dark brown-green colour.

In figs. 16 and 15 the thickened patches are of larger size and of greater opacity. The transparent parts seemed as if covered with an irregular film of pink jelly dotted over with little rounded heaps.

The bright gold and platinum paints made for ceramic gilding by the Gold und Silber Scheide Anstalt of Frankfurt, supply an excellent means of obtaining continuous films of almost any thickness. In these paints the metal has been brought into perfect solution in an essential oil. A plate of glass or of mica is smoothly coated with the paint, which is allowed to dry naturally. It is then heated in an air bath to about 400°, when the solvent oil and other volatile constituents are driven off and a smooth bright metallic film is found firmly adhering to the glass. At this stage the film is translucent and green by transmitted light. If the film is kept at a higher temperature for some time it becomes more transparent, and the colour by transmitted light changes to blue or purple. By long continued heating the film assumes a frosted appearance by reflected light, and the colour becomes paler by transmitted light.

These films are sometimes blistered by air bubbles, and an excellent idea of their continuity and transparence is obtained by carefully examining the spot where a bubble has been formed. So horn-like and translucent are these films that it was at first assumed that the paint contained a binding flux or frit, but, on careful inquiry I was assured by Dr. Fritz Roessler, the scientific director of the Frankfurt Works, that the films left on the glass are pure gold and platinum and free from any flux or frit. Fig. 14 is a gold film of this kind which has been annealed to the purple stage.

The thickness of a similar film was estimated by weighing the gold from a given area. Assuming that the density of the gold in this form is normal, the thickness was 166  $\mu\mu$ , or about twice the thickness of a gold leaf. Under the microscope the thickness, as seen at bubbles and broken edges, seemed to be much greater than this.

The phenomena of annealing are equally well seen in silver leaf and in films of silver chemically deposited on glass. In the case of silver, annealing takes place at the comparatively low temperature of 300° to 350°.

When the films are very thin the granular aggregations are not visible by transmitted light. As the thickness increases, the aggregations increase in distinctness, and are seen to be brown by transmitted light. The very feeble metallic reflection of these brown granules is noteworthy.

Tests of the electrical conductivity of films of gold and silver, before and after annealing, have been made for me at the National Physical Laboratory, the following is quoted from the report of the Director :—

"The tests were made on three kinds of films, viz. :—

"(A) Silver leaf on glass or mica.

"(B) Chemically deposited silver on glass.

"(C) Gold on glass or mica (applied in oil and reduced by heat).

"The general result of heating these films to temperatures above 300° C. was ultimately to increase their resistance from relatively small values (of the order of 0·2 to 50 ohms) up to very high values (thousands of megohms).

"It was also noticed, in the case of the chemically deposited silver, that the first heating seemed to produce a considerable fall of resistance (*e.g.*, from 14 ohms down to 2 ohms). Part of this change may have been due to the possibility of making better contacts after the heating.

"The following description of the specimens sent herewith will illustrate this general result.

"(A) Silver Leaf.

| No. | Description.                 | Treatment.                       | Resistance.                  |
|-----|------------------------------|----------------------------------|------------------------------|
| 2   | Specimens on glass .....     | Not heated                       | 0·16 ohm.                    |
|     | On glass (7·5 cm. × 3·5 cm.) | Heated about 1 hour<br>300° C.   | 0·9 "                        |
| 8   | " "                          | Further heating above<br>300° C. | Over 1,000,000 meg-<br>ohms. |
| 9   | On mica .....                | Further heating above<br>300° C. | Over 1,000,000 meg-<br>ohms. |

"(B) Chemically deposited Silver.

|    |                              |                                                |                                                       |
|----|------------------------------|------------------------------------------------|-------------------------------------------------------|
| 18 | On glass (7·5 cm. × 2·5 cm.) | Not heated .....                               | 15 ohms.                                              |
| 15 | " "                          | Heated to 300° C. ..                           | 2·1 "                                                 |
| 14 | " "                          | Heated higher .....                            | Over 1,000,000 meg-<br>ohms.                          |
| 14 | " "                          | Before heating ....                            | 11 ohms.                                              |
| 16 | " "                          | One end more highly<br>heated than the<br>rest | End over 1,000,000<br>megohms, re-<br>mainder 8 ohms. |

"(C) Gold.

|                 |                               |                                 |                               |
|-----------------|-------------------------------|---------------------------------|-------------------------------|
| 13              | On glass (4 cm. × 1·1 cm.) .. | Heated to complete<br>reduction | 6 ohms.                       |
| 17              | " "                           | Heated above 400° C.            | Over 1,000,000 meg-<br>ohms.  |
| 11<br>and<br>12 | On mica .....                 | Ditto .....                     | Over 1,000,000 meg-<br>ohms." |

"Calculating from the ordinary conductivity of silver, a film 7 cm. long  $\times$  3.5 cm. broad, having a resistance of 3 ohms, would have a thickness of 0.00001 mm. (100  $\mu\mu$ )."

Fig. 14 is a photograph of the actual film, No. 11, of the foregoing report.

Figs. 29 and 30 are photographs of the silver film, No. 14 (Bushy), by transmitted and by oblique light. The vertical band on these figures is the result of a needle scratch, which has uncovered the glass.

Neither in the case of the chemically deposited silver, nor in that of the gold paint, was there anything to suggest such complete discontinuity as the electrical tests would lead one to expect. In the gold film, especially, there appeared to be such a depth of granules in the film as would, even with the most open packing, supply a conductor of fair average cross-section. The under side of the film, examined through the glass or mica, appeared continuous, and closely adherent to its support.

Further experiments on electrical conductivity of annealed metals are now in progress.

Dr. Glazebrook has directed my attention to papers by A. C. Longden\* on "Electrical Resistance of Thin Films, deposited by Kathode Discharge." According to Mr. Longden, it was found that thin films had a negative, while thick films had a positive temperature coefficient.

These conclusions obviously do not apply to annealing temperatures used in my experiments, the increase of resistance in the Bushy tests being of an altogether different order from that referred to by Mr. Longden.

When a gold leaf laid on glass by Faraday's method is exposed for a very short time to mercury vapour, minute globules of mercury condense on the surface and, amalgamating with the gold, form transparent spots. This transparency quickly spreads and the whole leaf becomes almost as transparent and free from metallic reflection as if it had been annealed by heat. When the operation is watched with the microscope the mercury is seen shooting in thin streams between the plies and folds of the gold leaf. The final effect is similar to that obtained by heat annealing; there is the same transparent granulated film covering the glass, while the thicker brown-green aggregations form a skeleton outline of the ribs and markings of the leaf. Fig. 28 is a photograph near the edge of the leaf. Outside the edge and on the right is the uncovered glass surface with globules of mercury dotted over it.

If the mercury-treated leaf is heated sufficiently to drive off the mercury a very transparent film of annealed gold is left behind.

\* 'Physical Review,' pp. 40 and 84 (11), 1900, and p. 355, Dec., 1902.

In the first part of this paper it was shown that when the surface of metals is subjected to various forms of mechanical treatment a distinct covering film or layer is produced, which is in many respects different from the mass of metal below. By the regulated action of solvents this covering film can be wholly or partially removed. The observations now to be described show that the behaviour of this covering film under the action of heat annealing is in many respects analogous to that of thin films supported on glass.

For the study of these surface effects plates of pure gold were used. These were planished by beating on a polished surface, and polished by rubbing them lightly on rouged leather. The difficulty of obtaining a scratchless, uniform surface in a soft metal like pure gold is very great, but, fortunately for the purpose in view, a perfect surface was not needed, indeed the presence of lines of flow was sometimes an advantage.

Fig. 19 shows the surface of the polished plate. This and the three following figures are direct photographs without enlargement, by normally reflected light, with a 3 mm. oil immersion apochromat of 1.4 N.A. the magnification is  $\times 1500$ .

Fig. 20 is the same plate after heating to between  $700^{\circ}$  and  $800^{\circ}$  for 10 minutes. The surface film has become detached and broken up, evidently by the escape of air which had been imprisoned during the planishing and polishing operations. The surface has a viscous appearance and the holes made by the escaping gas add to this effect.

Fig. 21 is the same plate after further heating for an hour. The surface film appears to be aggregating and subsiding into the mass of metal below.

Fig. 22 is the same after further heating for an hour. In this case, as exactly the same spot has been photographed as in the preceding figure, it is possible to trace the further subsidence and disappearance of the original surface film.

Fig. 23 is another specimen of polished gold after heating for 1 hour. The ruffled surface again shows the effects of escaping gas.

In Fig. 24, after a further hour's heating, the final subsidence and the viscous flow of the surface are clearly seen.

To complete the parallelism between the behaviour of thin films on glass and surface films on massive metal, a plate of polished gold was exposed for a short time to the action of mercury, which was then driven off by heat.

The exact nature of the change brought about by this treatment was at first both puzzling and obscure. The greatly increased absorption of light by the altered surface could not be accounted for on the mere supposition that it was a scattering effect due to the breaking-up of the surface, because there was evidently loss of light

not merely in one but in all directions. This loss pointed to increased absorption, and the first idea was that the escaping vapour had blown the molten alloy into multitudes of films so thin as to be devoid of reflecting power. But this view was not borne out by the behaviour under mercury treatment of films supported on glass. In their case it was found that the metal left, after the mercury had been driven off, had arranged itself in transparent granular forms of greatly diminished reflecting power (fig. 28). The loss of light then is mainly due to absorption by the more transparent metal, not to scattering by repeated reflection from films.

A knowledge of this fact is of value in interpreting the appearances presented by surfaces of gold etched by aqua regia or by chlorine. In this case also there is an immense loss of light, which cannot be caused by scattering reflection, and can only be due to increased absorption.

Fig. 25 is a spot on a gold plate which has been amalgamated with mercury and then heated. On the light part of the surface the mercury has acted very slightly, and the lustre of the original surface is not much diminished, though there has been sufficient action to bring about aggregation in rounded forms. On the dark part the action has gone deeper, and in consequence the amount of light which has escaped absorption has been insufficient to disclose the details of structure.

Figs. 26 and 27 are photographs of the light and dark parts at a higher magnification by the 3 mm. objective. In Fig. 27 the spots of light on the dark back ground are reflections from the tops of transparent or translucent granules of rounded form.

The foregoing observations on the effects of heat on thin films and on surface films show conclusively that considerable molecular rearrangement is brought about at a temperature very much below the melting point of the metal. The mere fact of there being a certain amount of freedom imparted to the molecules by heat is not surprising, in view of the well-established facts of segregation and crystal growth in masses of metal at temperatures much below their melting point. But that this freedom takes place under conditions which lead the solid molecules to behave like liquid molecules is both new and suggestive.

The appearance of viscous flow and the forms assumed by the surface film suggest neither segregation nor crystal growth, but they do strongly suggest the behaviour of a viscous fluid under the control of surface tension. It appears probable, therefore, that at the surface of a solid the crystallic force is controlled and kept in check, sometimes actually overpowered, by surface tension, although in the body of the metal the equally balanced molecular attractions do not actually oppose the crystallic.

If the foregoing views are correct, it will follow that a freely suspended aggregate of solid molecules will take the spherical form if its surface is sufficiently large compared with its mass. A globule will only take the external form of a crystal when its mass becomes large enough to permit the crystalline force to overpower surface tension. The researches of Neville and Heycock\* have shown that, even in the solid state, the larger crystals grow at the expense of the smaller and eventually swallow them up. The range of the crystalline force therefore widens as the mass of the crystal is increased, while the range of the molecular forces remains constant. It seems possible, therefore, that the average size of the granules in solids may result from the establishment of a state of equilibrium between these rival forces.

The bearing of these views on the theory of the formation of globular precipitates and the spherocrystals described by Quincke† is obvious. The oily drops of calcium carbonate, which are seen as a first stage in the development of crystals, are not necessarily a super-saturated solution of calcium carbonate, they may be aggregates of solid molecules under the control of surface tension.

Mr. F. H. Neville has directed my attention to Faraday's observations‡ on the fluidity of minute globules of sulphur at the ordinary temperature. These observations seem to support the views I have advanced here.

Metals slowly deposited from solution tend to aggregate in the granular form. If the deposition takes place on nuclei floating in the solution or resting on the submerged surfaces, spheroidal granules are produced. If the deposition takes place on a clean smooth surface a thin flat film is produced, but even then the deposit is made up of flattened granules or "spicules" as I have called them in a former paper. When the thin film is annealed by heating, the flattened granules are drawn up into more distinctly rounded forms.

The flattened granule or "spicule" can be detected by oblique illumination even when it is too thin to show by transmitted light. By comparing its size and appearance under different forms of illumination when it is sufficiently massive to show by transmitted light, we are enabled to feel some confidence in the reality of those appearances which can only be seen by oblique illumination.

In the separation of solids directly from the gaseous state, *e.g.*, lamp black or magnesium oxide, the granular form is assumed by the molecular aggregates.

The more detailed study of these granular and spicular appearances will be dealt with in a further communication.

\* 'Roy. Soc. Proc.,' vol. 69, p. 325.

† 'Ann. d. Physik,' vol. 7, pp. 681—682, 1902.

‡ 'Quarterly J. of Science,' vol. 21, p. 392.



DESCRIPTION OF PLATES 11—13.

(The numeration of the figures is continued from those in foregoing paper.)

PLATE 11.

Fig. 13.—Gold leaf annealed by heating on glass.

Transmitted light with green screen.

Objective 12 mm. Apo. N.A. 0.65.

Magnification  $\times 440$ .

Fig. 14.—Gold paint on glass annealed by heating.

Light and objective as in fig. 13.

Magnification  $\times 440$ .

Figs. 15 to 18.—Gold film, phosphorus—reduced—annealed by heating on glass.

Transmitted light with green screen.

Objective 12 mm. Apo. N.A. 0.65.

Fig. 15.—The thickest part of the film. Fig. 16.—A thinner part.

Fig. 17.—A still thinner part. Fig. 18.—The thinnest part. The dark patches were deep green, and the light patches pale pink by transmitted light.

PLATE 12.

Fig. 19.—Gold plate planished and polished.

Normally reflected light, green screen.

Objective 3 mm. Oil immersion. Apo. N.A. 1.4.

Magnification  $\times 1500$ .

Fig. 20.—The same after heating for 10 minutes to  $700^{\circ}$ — $800^{\circ}$ .

Surface broken up into films by escaping gas.

Fig. 21.—The same after further heating for 1 hour.

Surface subsiding after escape of gas.

Fig. 22.—The same, after further heating for 2 hours.

Surface further subsided.

Fig. 23.—Gold plate, another specimen, heated for 1 hour.

Surface subsiding after escape of gas.

Lighting and objective as in figs. 19—22.

Magnification  $\times 1500$  (enlarged from 775).

Fig. 24.—The same after further heating for 1 hour.

The surface has subsided and has assumed an appearance of viscous flow.

PLATE 13.

Fig. 25.—Gold plate. A spot amalgamated with mercury, which was then driven off by a gentle heat. The dark part was most affected by the treatment, and the light part least.

Normally reflected light, green screen.

Objective 12 mm. Apo. N.A. 0.65. Magnification  $\times 250$ .

Fig. 26.—The light part of the same more highly magnified.

Objective 3 mm. Oil immersion. Apo. N.A. 1.4.

Magnification  $\times 775$ .

Fig. 27.—The dark part of the same more highly magnified.

Objective as in fig. 26. Magnification  $\times 775$ .

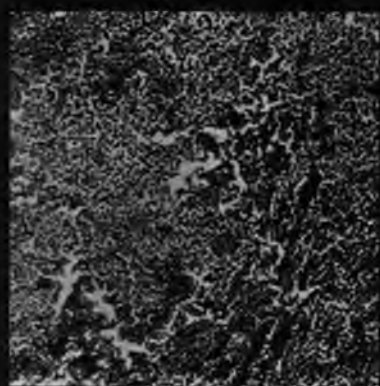


FIG. 13

X 440

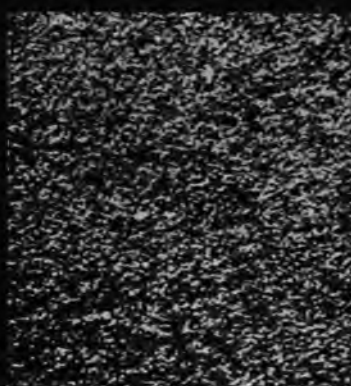


FIG. 14

X 500

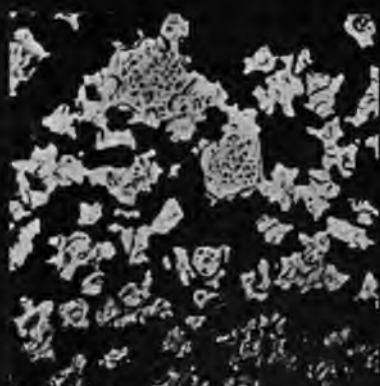


FIG. 15

X 440

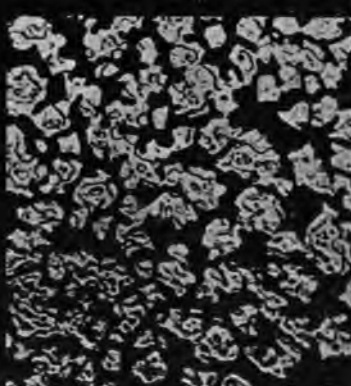


FIG. 16

X 440

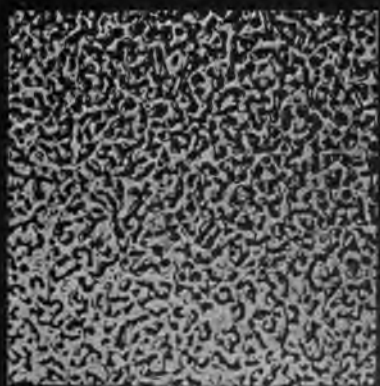


FIG. 17

X 440

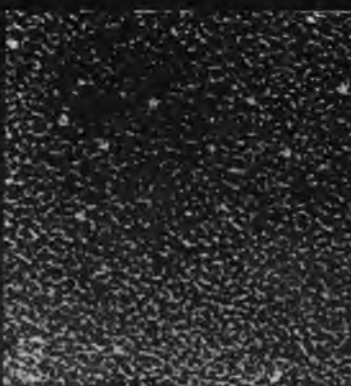
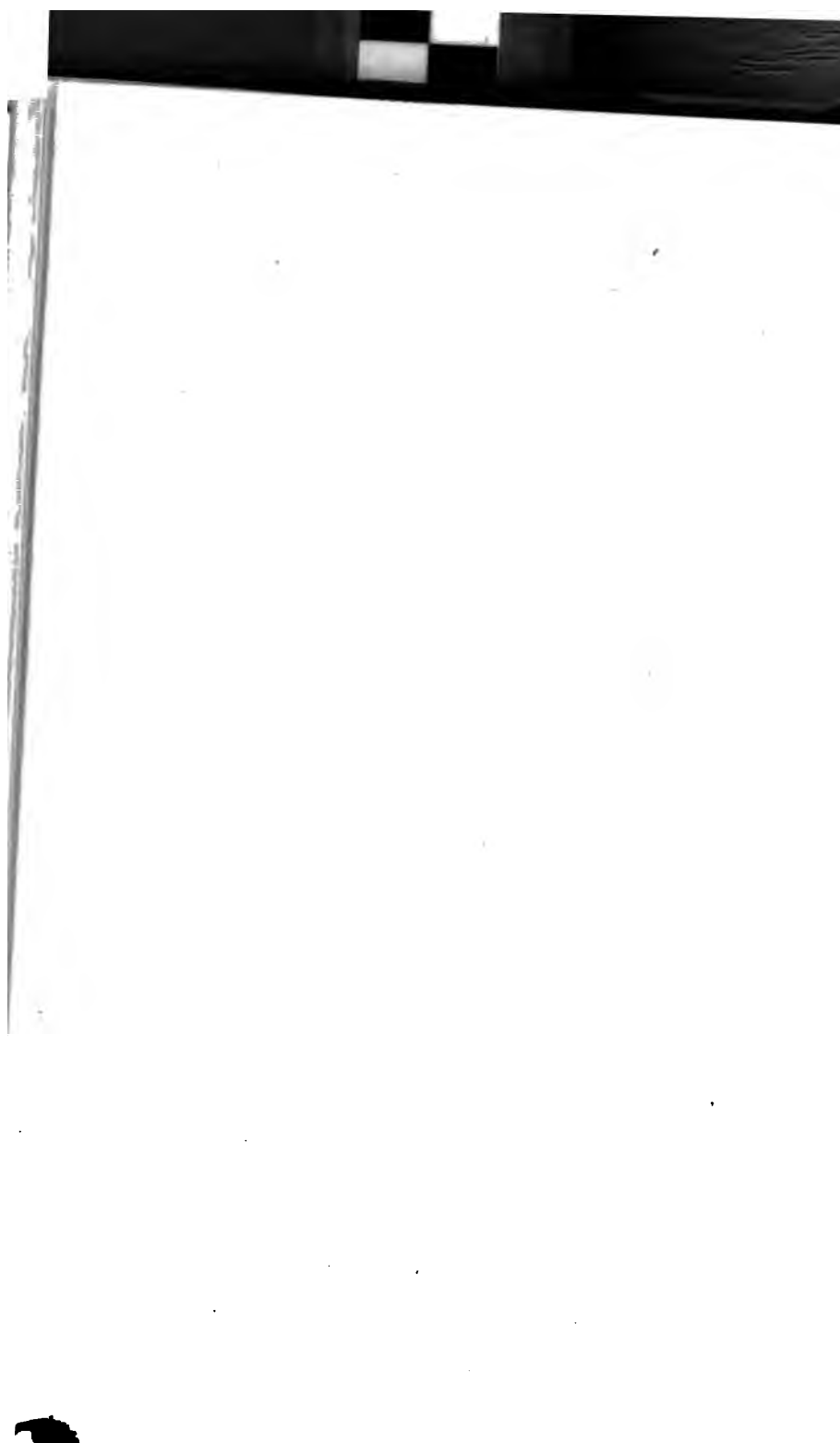


FIG. 18

X 440



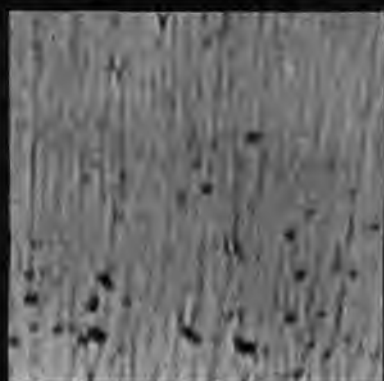


FIG. 19

X1500

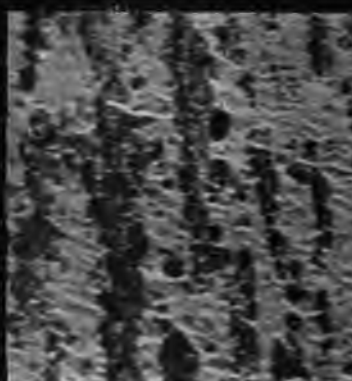


FIG. 20

X1500

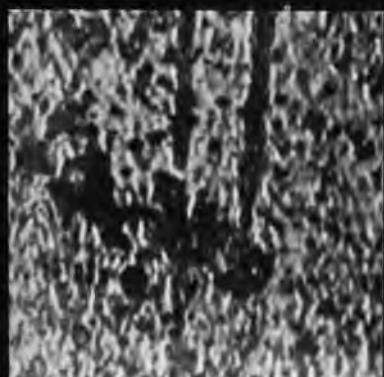


FIG. 21

X1500

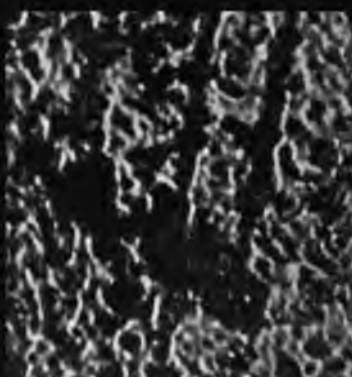


FIG. 22

X1500

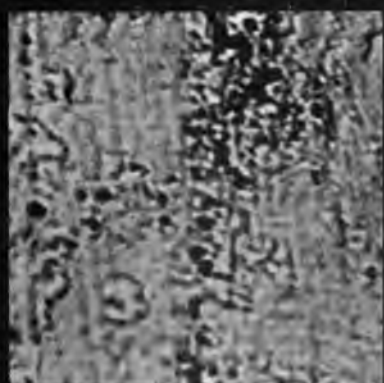


FIG. 23

X1500

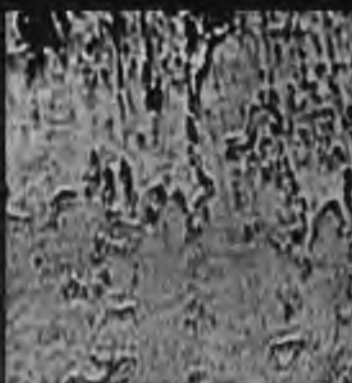


FIG. 24

X1500



1000

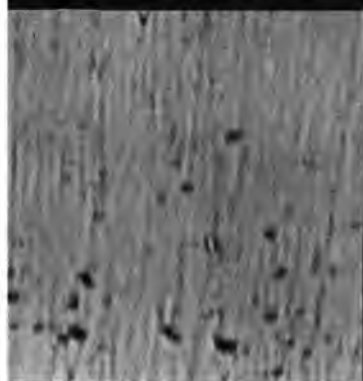


FIG 19 X1500

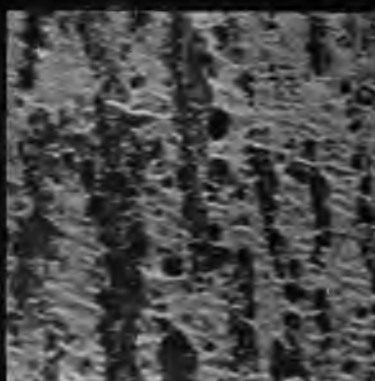


FIG 20 X1500



FIG 21 X1500

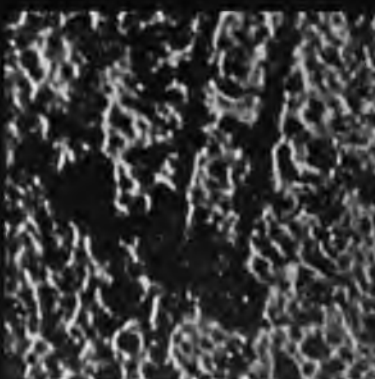


FIG 22 X1500

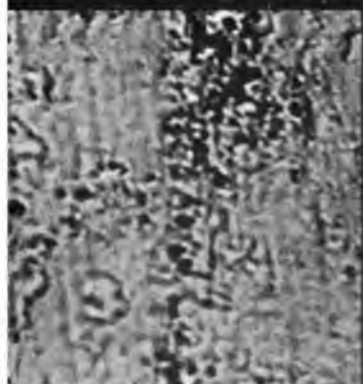


FIG. 23 X1500

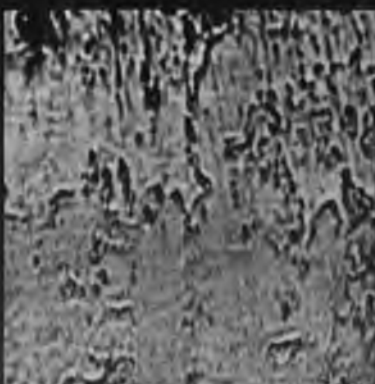


FIG. 24. X1500



1. The first part of the document is a list of names and titles, including "The Hon. Mr. Justice" and "The Hon. Mr. Justice".

2. The second part of the document is a list of names and titles, including "The Hon. Mr. Justice" and "The Hon. Mr. Justice".

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Fig. 28.—Gold leaf on glass, exposed to mercury vapour, and then heated sufficiently to drive off the mercury.

Transmitted light, green screen.

Objective 12 mm. N.A. 0·65. Magnification  $\times 440$ .

The dark patches were deep green, and the clear parts between them were colourless.

Fig. 29.—Silver film on glass, annealed by heating at  $350^{\circ}$ .

Transmitted light with green screen.

Objective 12 mm. N.A. 0·65. Magnification  $\times 440$ .

Fig. 30.—The same by dark ground illumination.

(Oblique transmitted light).

Objective 16 mm. N.A. 0·3. Magnification  $\times 440$ .

"The 'Hunting' of Alternating-Current Machines." By BERTRAM HOPKINSON, M.A. Communicated by Professor J. A. EWING, F.R.S. Received June 16,—Read June 18, 1903.

Many years ago the late Dr. John Hopkinson showed that if a pair of alternating-current dynamos, A and B, mechanically separate but connected electrically in parallel, be running steadily on a constant load and with a constant driving power, and if the steady motion be slightly disturbed, say by momentarily retarding A, then A will do less and B more than its share of the work, with the result that there will be a balance of force tending to accelerate A and to retard B and so to restore the state of steady motion. In other words the two machines tend to keep in step. Similar considerations apply to a synchronous alternating-current motor worked from supply mains—it tends to keep in step with the generators supplying it.

It has been found in practice that as a general rule the paralleled alternators do keep in step, but in a not inconsiderable number of cases great trouble has been caused by a tendency in the machines to develop gradually increasing oscillations about the state of steady motion in which they are in step with one another. This oscillation or "hunting" leads to violent cross magnetising currents, and sometimes the machines drop out of step altogether. This phenomenon has received a great deal of attention from the practical side, the object being of course to put an end to it. This experimental study has resulted in empirical rules as to fly-wheel effect, and in the various damping devices or "Amortisseurs" which are now largely used on alternating-current machinery and generally give satisfactory parallel running.

Theoretical treatment of hunting has been confined (so far as I am



aware) to the work of Kapp, and of others on similar lines,\* who have ascribed it to resonance. Take the case of a synchronous alternating current motor driven from a source of alternating E.M.F. of constant amplitude and periodicity. In all essentials this is the same problem as that of one alternating machine running in parallel with a number of others, but the results are simpler to express. The motor is supposed to work against a constant resistance, and corresponding to that resistance there will be a certain state of steady motion in which the motor runs with a constant speed equal to that of the generators supplying it and with a constant lag  $e$  behind them, and develops a torque  $T$  corresponding to the external resistance. If the angle of lag be increased to  $e + \xi$ , the torque will be increased to  $T + \frac{dT}{de} \xi$ , and if the external work done by the machine remains the same there will be a force  $\xi \frac{dT}{de}$  or  $c\xi$  tending to accelerate the motor. Kapp's argument then is that the equation of motion of the motor is  $M\ddot{\xi} + c\xi = 0$ , where  $M$  represents on a suitable scale the moment of inertia of the motor, from which it follows that it executes simple harmonic oscillations of constant amplitude and period  $2\pi\sqrt{(M/c)}$  about the state of steady motion. It is easy to calculate  $c$  approximately from a knowledge of the magnetic properties of the machine. Kapp worked out the period and found it to agree fairly well with observation in certain cases. He ascribed hunting to approximate equality between the period of free oscillation and that of some variation in the turning moment of the engine. Such equality would of course give rise to forced oscillations quite out of proportion to the cause. It was stated in support of this explanation that in certain cases an increase in the fly-wheel effect of the machine—viz., an increase in the period of oscillation—was found to aggravate the evil, contrary to what would at first sight be expected. And indeed it is probable that some cases of hunting are due to resonance.

I believe, however, that there have been cases in which it has been difficult or impossible to discover any external disturbing cause of approximately the same period as that of the oscillation. One case of the kind has come under my notice. A small single-phase synchronous motor, to be presently described, hunted violently under certain conditions when worked off the Wimbledon supply mains. The period of the oscillations could be varied continuously from about 0.35 to 0.45 second by appropriate variation of the self-induction in series with the motor. Furthermore, the hunting occurred equally, and with the same period, with either of two different generators working in the Power Station, one being three times the size of the other. It was

\* See 'Dynamomaschinen für Gleich- und Wechselstrom,' von Gisbert Kapp, p. 421; also a paper by Hans Görges, 'Elektrotechnische Zeitschrift,' vol. 8, 1900.

clear, therefore, that in this case at any rate the hunting was not due to resonance but to some essential instability in the motion of the motor itself.

It is easy to see how such instability could arise. In the argument given above it has been assumed that the torque is dependent only on the relative position of motor and generator and not on their relative velocity. As a matter of fact there is a term in the torque dependent on the velocity, and the equation of motion is  $M\ddot{\xi} + b\dot{\xi} + c\xi = 0$ . Higher differential coefficients than the second may and in fact do come in, but these are the most important terms as a rule. The solution of this equation is, if  $b$  is small,

$$\xi = \xi_0 e^{-b/2M} \sin \left[ \sqrt{\left(\frac{c}{M}\right)} t + \eta \right].$$

If  $b$  be positive, the amplitude of the oscillations continually decreases. If, however,  $b$  were negative, even though very small, the oscillations would continually increase and the motion be essentially unstable. Most dynamical systems are affected with viscosity, in which case  $b$  is positive, but systems are not unknown in which the contrary is the case. Watt's Governor is such a system.\* Its oscillations about steady motion are given by a cubic equation, the two complex roots of which have positive real parts and correspond to constantly increasing oscillations. There is no doubt that the motion of a synchronous motor is under certain conditions another instance of the same thing.

Suppose for the present that the motor has a permanent magnet or saturated field, and that it is working against a constant load.

Let  $\theta$  be an angle defining the position of the armature in space,  $I = A \sin \theta$  the induction linked with the field coils and with the armature when in position  $\theta$ . In virtue of the above assumption,  $A$  is constant. Let  $t$  be the time, and  $E \cos pt + F \sin pt$ , the E.M.F. of the source of supply;  $L$  the self-induction and  $\rho$  the resistance of the armature and any conductors in series with it.

Assuming for the moment that the motor is moving with uniform angular velocity, let  $u = \alpha_0 \sin pt + \beta_0 \cos pt$  be the current in the armature. The epoch of  $t$  is as yet unchosen; choose it so that in the steady motion  $\theta = pt$ . Now suppose that the state of steady motion is slightly disturbed so that the motor oscillates about it. Then we have in the disturbed motion:

$$\theta = pt + \xi \quad \text{and} \quad u = (\alpha_0 + \alpha) \sin pt + (\beta_0 + \beta) \cos pt,$$

where  $\xi$ ,  $\alpha$ ,  $\beta$  are small quantities varying periodically with the time. Experience shows that in all cases the period of the variation is long

\* See Routh's 'Rigid Dynamics,' vol. 2 (1892), p. 74; also Maxwell's *Collected Papers*, vol. 2, p. 106.

compared with  $2\pi/p$  the period of the alternating current. The external E.M.F. remains the same— $E \cos pt + F \sin pt$ —the induction  $A \sin \theta$  is also undisturbed by the oscillation.

Forming the equation for the E.M.F. at the terminals of the motor in the usual way and equating it to the impressed E.M.F. we find :

$$\begin{aligned} E \cos pt + F \sin pt &= \rho u + L \dot{u} + \frac{dI}{dt} \\ &= \rho \{(\alpha_0 + \alpha) \sin pt + (\beta_0 + \beta) \cos pt\} \\ &\quad + Lp \{(\alpha_0 + \alpha) \cos pt - (\beta_0 + \beta) \sin pt\} \\ &\quad + L \dot{\alpha} \sin pt + L \dot{\beta} \cos pt \\ &\quad + A(p + \dot{\xi}) \cos (pt + \xi). \end{aligned}$$

This equation is rigorously accurate under the assumptions proposed. Now equate the coefficients of  $\cos pt$  and  $\sin pt$  on the two sides, neglect products of the small quantities  $\alpha, \beta, \xi, \dot{\alpha}$ , etc., and separate the large terms corresponding to steady motion and the small terms corresponding to disturbed motion in the usual way.

Thus for steady motion

$$E = \rho \beta_0 + Lp \alpha_0 + Ap, \quad F = \rho \alpha_0 - Lp \beta_0,$$

and for the disturbed motion

$$L \dot{\alpha} + \rho \alpha - Lp \beta - Ap \xi = 0 \dots\dots\dots (1),$$

$$Lp \alpha + L \dot{\beta} + \rho \beta + A \dot{\xi} = 0 \dots\dots\dots (2).$$

The torque developed by the motor is

$$\begin{aligned} u \frac{dI}{d\theta} &= A \cos \theta \{(\alpha_0 + \alpha) \sin pt + (\beta_0 + \beta) \cos pt\} \\ &= A \cos (pt + \xi) \{(\alpha_0 + \alpha) \sin pt + (\beta_0 + \beta) \cos pt\} \\ &= \frac{1}{2} (A \beta_0 + A \beta - A \alpha_0 \xi) + \text{terms of period } \pi/p \text{ and quicker period,} \end{aligned}$$

again neglecting products of the small quantities. The large part of this,  $\frac{1}{2} A \beta_0$ , is equal to the constant resistance, the small balance is available for accelerating the motor. Thus the third equation is obtained :

$$2M \ddot{\xi} + A \alpha_0 \xi - A \beta = 0 \dots\dots\dots (3).$$

To solve equations (1), (2), and (3), we write as usual  $\alpha = P e^{xt}$ ,  $\beta = Q e^{xt}$ , and  $\xi = R e^{xt}$ , and so get, after substitution and elimination of  $P, Q$ , and  $R$ ,

$$\begin{vmatrix} Lx + \rho & -Lp & -Ap \\ Lp & Lx + \rho & Ax \\ 0 & A & -(A\alpha_0 + 2Mx^2) \end{vmatrix} = 0,$$

which reduces to

$$(A\alpha_0 + 2Mx^2) \{(Lx + \rho)^2 + L^2p^2\} + A^2L(x^2 + p^2) + A^2\rho x = 0 \dots (4)$$

The condition of stability of motion is, as explained in works on dynamics, that the real roots of this equation shall be negative, and that the real parts of the complex roots shall be negative. The criterion for this can be written down,\* but in this case it is simpler to proceed by approximation. It is known that  $x$  is a small quantity, the period of the oscillation we are investigating being in any practical case at least fifteen times that of the alternating current. Neglect  $x/p$  and  $x\rho/Lp^2$  therefore altogether in the first instance. Thus we obtain

$$(A\alpha_0 + 2Mx^2)(L^2p^2 + \rho^2) + A^2Lp^2 = 0,$$

whence

$$x = i\sqrt{\left\{ \frac{1}{2M} \left( A\alpha_0 + \frac{A^2Lp^2}{L^2p^2 + \rho^2} \right) \right\}} = i\delta, \text{ suppose.}$$

so that to this order of approximation the motor executes simple harmonic oscillations of constant amplitude and period  $2\pi/\delta$ . This, subject to an approximation which holds good in practical cases, is the result obtained by Kapp. Now, suppose that  $x = \gamma + i\delta$ , and substitute in the original equation (4). Neglect  $\gamma^2$ ,  $x^2/p^2$ , and  $\gamma/p$ , but keep  $x/p$ ,  $x\rho/Lp^2$ , etc.

The result is

$$4M\gamma i\delta(L^2p^2 + \rho^2) + (A\alpha_0 - 2M\delta^2)2Li\delta\rho + A^2\rho i\delta = 0,$$

\* The condition that the real roots and the real parts of the complex roots of the biquadratic

$$ax^4 + bx^3 + cx^2 + dx + e = 0$$

shall all be negative is that the quantity

$$bcd - ad^2 - eb^2,$$

and the coefficients  $a, b, c, d, e$  shall all have the same sign (see Routh's 'Rigid Dynamics' (1892), vol. 2, p. 192). In the case of the biquadratic here treated, this condition reduces to

$$2A(2L\alpha_0 + A) - \frac{8M}{L}(L^2p^2 - \rho^2) > 0,$$

which is equivalent to the condition  $Lp < \rho$  found later on, if, as is the fact, the first term can be neglected in comparison with the second.

whence

$$\begin{aligned}
 4M\gamma &= -\frac{A^2\rho + (A\alpha_0 - 2M\delta^2)2L\rho}{L^2p^2 + \rho^2} \\
 &= -\frac{\rho}{L^2p^2 + \rho^2} \left( A^2 - \frac{A^2Lp^22L}{L^2p^2 + \rho^2} \right) \\
 &= \rho A^2 \frac{L^2p^2 - \rho^2}{(L^2p^2 + \rho^2)^2} \dots\dots\dots (5)
 \end{aligned}$$

If, therefore,  $Lp > \rho$ , as is nearly always the case,  $\gamma$  is positive, and the motion is unstable, the oscillations if once started continually increasing in amplitude according to the law  $e^{\gamma t}$ .

In the above it has been assumed that the field is unaffected by the oscillations, remaining the same in the disturbed as in the steady motion. As a matter of fact this is not usually the case, the field is disturbed by the oscillation owing to the varying armature reaction. The general effect is easily expressed thus. The induction linked with armature and field coils in the steady motion is supposed, as before, to be  $A \sin \theta$ . In the disturbed motion the field is slightly altered in amount, and slightly distorted, in a periodic way, and becomes  $I = (A + a) \sin \theta + b \cos \theta$ , where  $a$  and  $b$  are small quantities dependent on  $\alpha$ ,  $\beta$ , and  $\xi$ . Terms involving  $\sin 2\theta$  and  $\cos 2\theta$  will also appear to some extent, but may for practical purposes be neglected. The current in the armature is

$$\begin{aligned}
 u &= (\alpha_0 + a) \sin pt + (\beta_0 + \beta) \cos pt \\
 &= (\alpha_0 + a) \sin (\theta - \xi) + (\beta_0 + \beta) \cos (\theta - \xi) \\
 &= \alpha_0 \sin \theta + \beta_0 \cos \theta \\
 &\quad + (\alpha + \beta_0\xi) \sin \theta + (\beta - \alpha_0\xi) \cos \theta,
 \end{aligned}$$

and the general effect of the varying current on the field is that

$$a = \kappa (\alpha + \beta_0\xi), \quad b = \lambda (\beta - \alpha_0\xi),$$

where  $\kappa$  and  $\lambda$  are constant for any given state of steady motion.  $\kappa$  represents the change in total induction produced by varying the "wattless" component of the current, and  $\lambda$  the change in distortion produced by varying the other component. Taking these expressions for the induction, it is easy to find the time of oscillation and rate of increase as in the simpler case investigated above. It will suffice here to give the results. The period of the oscillation is  $2\pi/\delta$ , where

$$2M\delta^2 = +A\alpha_0 - \lambda\alpha_0^2 - \kappa\beta_0^2 + \frac{\{(A - \lambda\alpha_0)^2(L + \kappa) + \kappa^2\beta_0^2(L + \lambda)\} p^2}{(L + \kappa)(L + \lambda)p^2 + \rho^2},$$

and the amplitude increases at the rate  $e^{\gamma t}$ , where

$$\begin{aligned}
 4M\gamma &= \frac{\rho}{\{(L + \kappa)(L + \lambda)p^2 + \rho^2\}^2} \left[ p^2 \{(A - \lambda\alpha_0)^2(L + \kappa)^2 + \kappa^2\beta_0^2(L + \lambda)^2\} \right. \\
 &\quad \left. - \rho^2 \{(A - \lambda\alpha_0)^2 + \kappa^2\beta_0^2\} \right] \dots\dots\dots (6).
 \end{aligned}$$

As a rule  $\kappa\beta_0$  is small compared to  $(A - \lambda\alpha_0)$ , so that the criterion of instability in this case is approximately  $(L + \kappa)p > \rho$ , and is generally fulfilled. The value of  $(L + \kappa)$ , which will not vary greatly with load, may be determined by observing the current given by the machine when short-circuited, including, of course, in its circuit all resistances and self-induction up to the constant source of E.M.F., which has been postulated. The apparent resistance under these circumstances is approximately  $\sqrt{([L + \kappa]^2 p^2 + \rho^2)}$ . On the other hand, the value of  $L$  may be approximately obtained by observing the current when the machine is at rest, and connected to the mains, the field coils being short-circuited. The apparent resistance of the whole circuit under these circumstances is  $\sqrt{([L^2 p^2 + \rho^2])}$ . If the motor be under-excited  $\alpha_0$  is positive.  $\beta_0$  is positive for a motor and negative for a generator. The E.M.F.  $Ap \cos pt$  is equal to the impressed E.M.F. less that required to drive the current through the self-induction and resistance of the circuit; hence, unless  $Lp$ , or  $\rho$ , or the current, be large,  $Ap/\sqrt{2}$  is not much different from the applied E.M.F.  $[\sqrt{(\text{mean}^2)}]$ . By reducing the exciting current  $Ap$  is somewhat reduced, owing to the increased armature current; but the reduction is far from being in proportion to the decrease in exciting current. On machines with large armature reaction and small self-induction,  $Ap$  is practically constant, and equal to  $\sqrt{2}$  times the impressed E.M.F.  $[\sqrt{(\text{mean}^2)}]$ .

### *Damping Coils.*

In practice there are, of course, many causes unconsidered in the above investigation which tend to damp out the oscillations, and which in all but exceptional cases overpower the forces making for instability, and render the motion stable. Air resistance and local currents in the armature give rise to forces of this nature, which increase roughly in proportion to the velocity and so appear in the equations of motion as true viscous terms. The most important damping effect, however, is that due to the variations of the field of the motor, which, as stated in the last paragraph, are generally produced by the oscillation. These variations give rise to periodically varying electric forces in the substance of the magnets and in the field coils, which cause currents in the former and variations of the current in the latter. These induced currents re-act on the armature, producing changes in the torque which tend to damp out the oscillations. In many machines the effect is intensified by putting additional damping coils of copper or "Amortisseurs," as they are called, round the field magnets. I propose shortly to investigate this damping effect.

The general effect of the induced currents in the magnets and in

their surrounding coils (whether damping coils or field coils)\* is equivalent to that of a circuit of a certain resistance  $R$  supposed to surround completely laminated magnets of the same size and shape magnetised by a constant field current. The induction linked with this circuit will be, taking the notation already used,  $\nu I$  or  $\nu (A + a)$ , where  $\nu$  is a constant. The current round the circuit, produced by the oscillation, is, therefore,  $-\frac{\nu}{R} \frac{dI}{dt}$ , or  $-\frac{\nu}{R} \frac{da}{dt}$ . This current tends to slightly demagnetise the magnets if  $a$  be increasing, and its effect on the induction linked with the field coils and armature may be represented by a term  $-\mu \frac{da}{dt}$ , where  $\mu$  is a positive constant. The quantity  $\mu$  is a time, it is the time in which the induction in the magnets falls to  $1/e$  of its initial value if the field coils be suddenly short-circuited. If the armature be forced to make small oscillations, given by  $\xi = \xi_0 \sin \delta t$ , about the state of steady motion, the induction will be as before (p. 240).

$$I = (A + a) \sin \theta + b \cos \theta,$$

where now, however,

$$a = -\mu \frac{da}{dt} + \kappa (\alpha + \beta_0 \xi) \dots\dots\dots (7),$$

while, as before

$$b = \lambda (\beta - \alpha_0 \xi).$$

The E.M.F. at the terminals of the motor is

$$\begin{aligned} E \cos pt + F \sin pt &= \rho u + L \dot{u} + \frac{dI}{dt} \\ &= \rho \{(\alpha_0 + \alpha) \sin pt + (\beta_0 + \beta) \cos pt\} \\ &\quad + Lp \{(\alpha_0 + \alpha) \cos pt - (\beta_0 + \beta) \sin pt\} \\ &\quad + (A + a) p \cos (pt + \xi) \\ &\quad - \lambda (\beta - \alpha_0 \xi) p \sin pt \\ &\quad + \left[ L \dot{\alpha} \sin pt + L \dot{\beta} \cos pt + A \dot{\xi} \cos pt \right. \\ &\quad \left. + \frac{da}{dt} \sin pt + \lambda (\beta - \alpha_0 \xi) \cos pt \right]. \end{aligned}$$

We drop the terms in square brackets, and investigate the damping effect of the "Amortisseur" coil separately as a small effect of the

\* It is worth noting here that the result, so far as damping is concerned, is the same whether the additional copper is put into a separate short-circuited winding or into the field coils. In the latter form it assists in reducing the ordinary losses in those coils.

same order of magnitude as the opposite effect which is dependent on those terms. The result is:

$$\rho\alpha - (L + \lambda)p\beta - A\rho\xi + \lambda\alpha_0\rho\xi = 0,$$

and

$$a\rho + L\rho\alpha + \rho\beta = 0,$$

whence

$$\{L(L + \lambda)p^2 + \rho^2\}\beta + L\rho^2(A - \lambda\alpha_0)\xi + a\rho\rho = 0,$$

and

$$\{L(L + \lambda)p^2 + \rho^2\}\alpha + a(L + \lambda)p^2 - \rho\rho(A - \lambda\alpha_0)\xi = 0.$$

These give  $\alpha$  and  $\beta$  in terms of  $\xi$  and  $a$ , and substituting in (7), we find

$$a \left\{ 1 + \frac{\kappa(L + \lambda)p^2}{L(L + \lambda)p^2 + \rho^2} \right\} + \mu \frac{da}{dt} = \xi_0 \sin \delta t \left\{ \kappa\beta_0 + \frac{\kappa\rho\rho(A - \lambda\alpha_0)}{L(L + \lambda)p^2 + \rho^2} \right\},$$

whence it follows that

$$a = a_0 \sin(\delta t + \epsilon),$$

where

$$\tan \epsilon = - \frac{\mu\delta}{1 + \frac{\kappa(L + \lambda)p^2}{L(L + \lambda)p^2 + \rho^2}} \quad \left. \vphantom{\tan \epsilon} \right\} (8).$$

and

$$a_0 \left\{ 1 + \frac{\kappa(L + \lambda)p^2}{L(L + \lambda)p^2 + \rho^2} \right\} = \kappa \left\{ \beta_0 + \frac{\rho\rho(A - \lambda\alpha_0)}{L(L + \lambda)p^2 + \rho^2} \right\} \xi_0 \cos \epsilon$$

The small periodic term in the torque, produced by the oscillation, is found, as before, to be

$$\frac{1}{2} \{a\beta_0 + (A - \lambda\alpha_0)\beta - (A - \lambda\alpha_0)\alpha_0\xi\}.$$

The value of this when  $t = 0$  or  $\xi = 0$ , that is when the motor is in the position of steady motion, though not moving with the steady velocity, is

$$\frac{1}{2} \left\{ a_0\beta_0 \sin \epsilon - (A - \lambda\alpha_0) \frac{\rho\rho a_0 \sin \epsilon}{L(L + \lambda)p^2 + \rho^2} \right\},$$

which from (8) is equal to

$$-\frac{1}{2} \frac{\kappa\xi_0\mu\delta \left[ \beta_0^2 - \frac{\rho^2\rho^2(A - \lambda\alpha_0)^2}{\{L(L + \lambda)p^2 + \rho^2\}^2} \right]}{\mu^2\delta^2 + \left\{ 1 + \frac{\kappa(L + \lambda)p^2}{L(L + \lambda)p^2 + \rho^2} \right\}^2} \dots\dots\dots (9).$$

The velocity at this moment is  $\left[ \frac{d}{dt} (\xi_0 \sin \delta t) \right]_{t=0}$  or  $\xi_0 \delta$ .

The oscillation about the state of steady motion is, therefore,



resisted by a force proportional to the excess of the actual velocity over that of the steady motion, or by a true viscous force, and the magnitude of the force is, in the simple case when  $\rho = 0$ ,

$$-\frac{1}{2} \frac{\kappa \mu \beta_0^2}{\mu^2 \delta^2 + (1 + \kappa/L)^2} \xi = -2M\gamma' \dot{\xi} \quad \dots\dots\dots (10).$$

Taking this force into consideration, as well as the similar force of opposite sign whose existence was proved in the first paragraph, we find finally that the free oscillations of the system are given by the equation :

$$\xi = \xi_0 e^{(\gamma - \gamma')t} \sin \delta t,$$

where  $\gamma$  and  $\gamma'$  have the following values nearly, if  $\rho$  is small,

$$\left. \begin{aligned} \gamma &= \frac{\rho A^2}{4M(L + \kappa)^2 p^2} \\ \gamma' &= \frac{\kappa \mu \beta_0^2}{4M \left\{ \mu^2 \delta^2 + \left(1 + \frac{\kappa}{L}\right)^2 \right\}} \end{aligned} \right\} \dots\dots\dots (11).$$

These results have been obtained for a single-phase motor, with a constant self-induction and a sine-wave E.M.F. A generator running in parallel with a number of others is, of course, covered by the same equations. The results are applicable, with slight modification, to a two-phase or three-phase machine, and it would be possible, if worth while, to find the alterations introduced by the varying self-induction and distorted wave-forms which exist more or less in all actual dynamos. In no case, however, could accurate quantitative results be arrived at without great labour, for the forces here investigated are small, and in actual work a great many small disturbing causes would have to be taken into account (such, for example, as small changes in the resistance overcome by the motor)\* before an accurate quantitative criterion of stability could be arrived at. A good deal of valuable information can, however, be got out of the equations as to the general effect upon stability of running of varying the constants of the machine.

(1)  $\gamma'$  diminishes as  $\delta$  increases or the damping increases with the period of the oscillation. Hence increased fly-wheel effect always results in better damping owing to the increase in the period. Increasing the self-induction has the same effect; and it also works in favour of stability by diminishing  $\gamma$ . A mere alteration of  $M$  without altering  $\delta$  has no effect because it alters  $\gamma$  and  $\gamma'$  in the same ratio.

(2) The damping is proportional to  $\kappa \beta_0^2$ . Now the steady torque is

\* A case of great practical importance, in which the changes of load can be calculated easily, is that of the rotary converter.

$\frac{1}{2} A \beta_0$ . Hence for a fixed field excitation the damping term is about proportional to the square of the load; the more the machines are loaded (within limits) the better they run in parallel. This is in accord with experience. Furthermore, with constant load,  $\beta_0$  is inversely proportional to  $A$ , and a reduction of  $A$  results in better damping. This I have also found to be true on the machine with which I experimented, viz.: that if with a constant load you diminish the field current you get more stable running.

(3) The co-efficient of instability, or  $\gamma$ , will in most cases (for which  $\rho$  is small compared with  $L\rho$ ) be proportional to  $\rho A^2$  and inversely proportional to  $L^2 \rho^2$ .

(4) If  $\mu$  be increased from zero, in other words if the resistance to the induced currents in and about the pole pieces be diminished, the damping effect corresponding to  $\gamma'$  first increases to a maximum and then diminishes. It is possible therefore to carry the application of "Amortisseurs" too far. That this is so is obvious when one considers that a coil of no resistance round the pole piece would completely destroy all variation of induction and all the damping effect which depends on such variations. It would in fact correspond to the case first investigated of a motor with a fixed field, or without armature reaction, which as shown is usually unstable.

(5) Referring to the general expression for  $\gamma'$  (equation 9) in which the resistance is taken into account, it appears that if  $\beta_0^2 < \frac{\rho^2 \rho^2 (A - \lambda \alpha_0)}{\{L(L + \lambda)\rho^2 + \rho^2\}^2}$ ,  $\gamma'$  becomes negative, and the damping coils, instead of reducing the oscillations, actually tend to increase them.

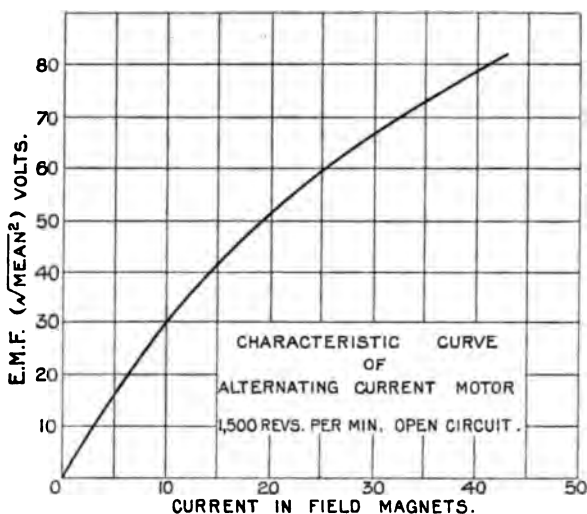
$\frac{(A - \lambda \alpha_0) \rho}{\sqrt{L(L + \lambda)\rho^2 + \rho^2}}$  is about equal to  $C(\sqrt{2})$ , where  $C$  is the current in the machine when standing and connected to the mains. The limits outside which  $\beta_0$  must lie in order that the damping coils may operate as such, and not as additional causes of instability, are therefore about  $\pm \frac{\rho}{L\rho} C(\sqrt{2})$ , and are very narrow in machines of any size. The matter only becomes practically important in the case of small machines, and of motors on long transmission lines. The behaviour of the small motor with which I experimented is considerably influenced in this way.

#### *Experimental Confirmation.*

I have in a general way confirmed the results here obtained by experiment on a small alternating current motor. This machine is a 4-pole generator, made by the Westinghouse Company, and intended to give an output of about 10 amperes continuous current at 110 volts. It was converted into a synchronous alternating current machine by fitting slip rings on to it.

The machine was separately excited, and the no-load characteristic curve for a speed of 1500 revolutions per minute is shown on fig. 1.

FIG. 1.

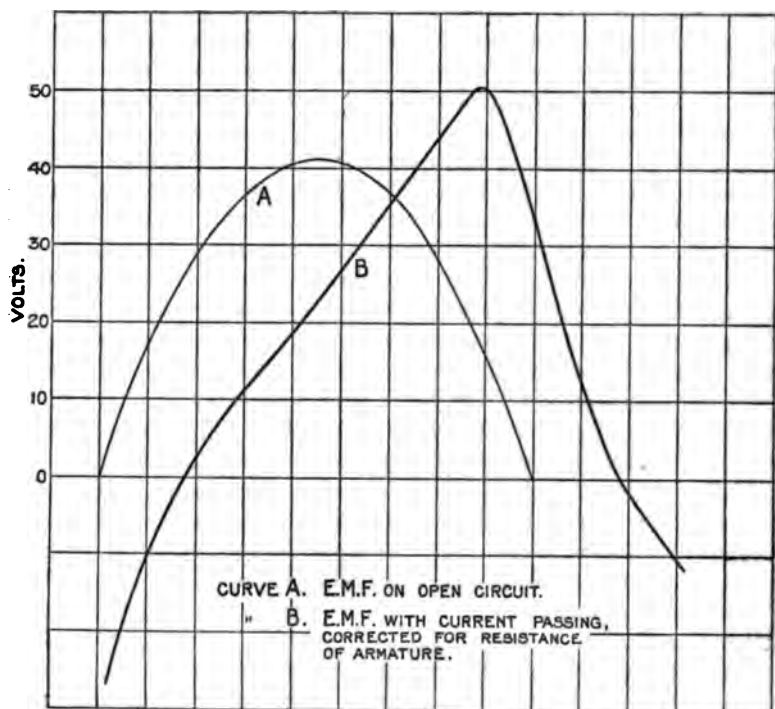


The currents are in arbitrary units, the potential is the square root of mean square of the alternating potential. The lower parts of the characteristic are a good deal affected by the previous treatment of the magnets; the curve gives average values. The machine gives, at no-load and at all excitations, very approximately a sine-wave of E.M.F., the actual value being  $E (\sin pt + \frac{1}{30} \sin 3pt + \text{terms of higher order})$ . With a heavy non-inductive load and low field, however, the field is a good deal distorted. In fig. 2 is shown the curve of E.M.F. of the machine when excited with a current of 10.5 and working as a generator on a non-inductive resistance amounting together with the armature resistance to 1.5 ohms.

The machine was worked off the local supply mains, which gave a potential of from 94—98 volts  $\sqrt{(\text{mean}^2)}$  with a frequency of 50 per second. The impressed E.M.F. is also approximately a sine-curve. The resistance and reactance ( $Lp$ ) of the transformer, mains to the power house, &c., were determined from the drop in pressure at the terminals when giving a heavy non-inductive and inductive current respectively. The resistance was equivalent to about 0.1 ohm in the motor circuit, the reactance to about 0.12 ohm. The pole-pieces of the machine are laminated and cast into a solid yoke.

The pole pieces are of  $2\frac{1}{2}$ -inch square section, and  $3\frac{1}{2}$  inches deep from the pole face to where they are set into the yoke. The diameter of the armature is  $5\frac{1}{2}$  inches.

FIG. 2.



Rough determinations were made of the various constants of the machine; the resistance measured in the ordinary way was found to be 0.55 ohm cold. In normal working the resistance averaged about 0.7 ohm, making a total of 0.8 ohm with the resistance in the mains. The self-induction  $L$ , or that part of the induction which is linked with the armature but not with the field coils, was measured by observing the drop of potential across the armature when passing an alternating current, the field coils being short-circuited so as to eliminate the induction linked with them. The apparent resistance was assumed to be  $\sqrt{(L^2 p^2 + r^2)}$ . The result was that  $Lp$  varied from 0.65—0.93 ohm, according to the position of the armature. We take 0.8 ohm as the mean value of  $Lp$ , making 0.92 ohm total reactance with the reactance in the mains. For the determination of  $\kappa$  the machine was run as a generator on various non-inductive resistances varying from nothing up to 3 ohms. It was assumed that if  $V$  be the open circuit potential,  $C$  the current [ $\sqrt{(\text{mean}^2)}$  in each case] and  $R$  the total resistance including armature, then  $V = C \sqrt{[(L + \kappa)^2 p^2 + R^2]}$ . So determined the value of  $(L + \kappa)p$  was found to range from 1.3 ohms in the first case (short circuit) to 1.1 ohms in the second.

This method of measurement is only strictly accurate if  $\kappa = \lambda$ , in which case the value of  $\kappa$  should appear constant for all resistances. For present purposes we may take the higher value 1.3 ohms (which is the more nearly accurate) as a good enough approximation for  $(L + \kappa)p$ , or 1.42 ohms if the additional reactance of the mains is included, and 0.5 ohm for  $\kappa p$ .

The power required to drive the motor unloaded against friction, hysteresis, etc. (taken as the applied watts less the  $C^2R$  losses in the armature), was found to average about 250 watts. This is the value of  $\frac{1}{2}Ap\beta_0$  in all cases when the motor is described as unloaded.

Finally the value of  $\mu$  was roughly determined in the following way:—The current was passed through the field coils, the machine being at rest and the circuit of the armature open. The field coils were short-circuited at a definite instant of time, and the current in them was measured at various times after the short-circuit took place. The short-circuiting was effected by means of a long heavy pendulum which closed a switch at the lowest point of its swing. The pendulum carried a contact maker which at a determinate later point in the swing connected a resistance included in the field circuit to an electrometer. The fall of potential in the resistance gave the current at the moment of making contact, and the time could be calculated from the length of the pendulum swing between closing the switch and making contact. It was found that with sufficient accuracy for present purposes the value of the current in the field magnets was halved in 0.07 second. Since in this case the current diminishes according to the law  $e^{-t/\mu}$ , it follows that  $\mu$  is about one-tenth of a second;  $\mu$  varies somewhat with the temperature of the field coils, etc., one-tenth can be taken as its order of magnitude.

Taking the above values of the constants, it appears that with the motor connected direct to the mains  $\gamma$  is negative. Furthermore, unless the machine is very much under-excited, we have

$$\frac{p\rho(A - \lambda\alpha_0)}{L(L + \lambda)p^2 + \rho^2} = 30\sqrt{(2)} \text{ ampères, roughly,}$$

taking  $60\sqrt{(2)}$  volts as a rough value for  $(A - \lambda\alpha_0)p$ ,  $\rho$  as 0.8 ohm, and  $\sqrt{[L(L + \lambda)]p}$  as 1 ohm, so that  $\gamma'$  is also negative unless  $\beta_0$  has a value comparable with  $30\sqrt{(2)}$  ampères. We should, therefore, expect this machine to be violently unstable. This was in fact, found to be the case; when connected direct to the mains as a motor with an exciting current of thirty or more the machine very rapidly developed oscillations, and finally dropped out of step altogether. The oscillations occurred just the same, whether a large or small generator was working at the Power Station. They were not affected by putting heavy rings of copper round the pole-pieces in addition to the field winding. It was only by reducing the field current to 13.5 and loading the machine

with a brake until the applied power was about 1800 watts that the "hunting" could be stopped.

[That the hunting in this case was principally due to the negative value of  $\gamma'$  was shown by the fact that it was not possible to stop the hunting by the introduction of external resistance. Even with a resistance amounting to 2.5 ohms, with which  $\rho$  would certainly be greater than  $(L + \kappa) p$ , the motion was still unstable. The impossibility of making the motion stable by adding resistance puzzled me considerably at first, as I had not noticed the importance of the negative term in  $\gamma'$ , but had treated it as a negligible quantity—*June 28th.*]

By inserting self-induction in series with the motor the violence of the "hunting" could be gradually diminished, and at the same time its period could be continuously increased from about 0.35 second to 0.45 second. When the self-induction was such that  $L\rho$  amounted to about 6 ohms the motion became stable, the oscillations when once started rapidly dying away. This is in accordance with conclusion (1) above, and the continuous variation of the period though the hunting continues is proof of the essential instability of the motion.

With external self-induction giving a total reactance of about 3 ohms and resistance of 1.2 ohms the stability depended on the load and on the exciting current. The following observations were made:—

(a) Exciting current 11.0, motor unloaded. The motion was stable, oscillations if started dying slowly away. Period of oscillation 0.42 second.

(b) Exciting current was increased to 18.5 when the motion became unstable. By loading the motor slightly with a brake the "hunting" could be stopped. Period 0.38 second.

(c) Exciting current increased to 30.5. The motion with the motor unloaded became violently unstable. By loading the motor with a brake until the power delivered to motor (excluding external self-induction) amounted to 1000 watts, the "hunting" could be stopped. It was curious to watch the effect of the load on the current taken by the machine. The ammeter had such a slow period that it could not follow the variations in current due to the oscillations, but remained steady, giving the average of the square of the current. When the machine was "hunting" the ammeter showed a current of about 27 amperes, and the wattmeter an applied power of about 710 watts, two-thirds of which were, of course, accounted for by the  $C^2R$  losses. On putting the load on, the current as shown by the ammeter gradually diminished until when the motion was steady it was 13.5 amperes. The power indicated by the wattmeter was now again about 1000 watts, but this time only about one-eighth was going in  $C^2R$  losses.

The last series of experiments is a good confirmation of conclusions

(2) and (5) above. It is worth while in this case, the conditions of which approximate to those assumed in the theory, to determine the order of magnitude of  $\gamma$  and  $\gamma'$ .

The following measurements were made :—

Total reactance ( $Lp$ ) varied between 2·81 and 3·18 ohms, according to position of armature. Its value may be taken as constant, and equal to 3 ohms without serious error.

Total resistance ( $\rho$ ) = 1·2 ohms.

In case (c) the potential across the motor terminals (that is excluding the external self-induction) was 75 volts. Hence,  $A_p$  is less than  $75 \sqrt{(2)}$  volts. On the other hand,  $A_p$  is greater than  $\sqrt{(2)}$  times the open-circuit potential of the machine with exciting current 30·5, which was measured and found to be 65 volts. Take, therefore  $A_p$  as equal to  $70 \sqrt{(2)}$ . The power supplied to motor terminals (again excluding the external self-induction) was 1000 watts. The current was 13·5 ampères, hence the  $C^2R$  loss in armature is 110 watts (armature resistance taken as 0·6 ohm), and we have

$$\frac{1}{2} A_p \beta_0 = 890 \text{ watts,}$$

and

$$\beta_0 = 12·7 \sqrt{(2)} \text{ ampères.}$$

Thus we obtain

$$4M\gamma\mu^2 = \frac{\rho A^2 \mu^2}{(L + \kappa)^2 p^2} = \frac{1·2 \times (70 \sqrt{2})^2}{(3·5)^2} = 960.$$

(See formula 11 above.)

For  $\gamma'$  the more accurate formula (9) must be taken, since, as in all experiments with this motor, the resistance term is important. The formula may be written with sufficient accuracy

$$4M\gamma'\mu^2 = \frac{\kappa \mu \mu^2 \left[ \beta_0^2 - \frac{\rho^2 A^2 \mu^2}{(L^2 \mu^2 + \rho^2)^2} \right]}{\mu^2 \delta^2 + (1 + \kappa/L)^2}.$$

We take  $\mu = \frac{1}{10}$  sec.,  $2\pi/\delta$  (the period of oscillation) = 0·36 second,  
 $\frac{2\pi}{p} = \frac{1}{50}$  second Hence  $\delta$  is 17 and  $p = 314$ .

We have

$$\frac{A p \rho}{L^2 p^2 + \rho^2} = \frac{70 \sqrt{(2)} \times 1·2}{10·4} = 8 \sqrt{(2)} \text{ ampères.}$$

Hence

$$4M\gamma'\mu^2 = \frac{0·5 \times 0·1 \times 314 [(12·7)^2 - (8)^2] \times 2}{[(0·1)^2 \times (17)^2 + (1·3)^2]} = 680.$$

This value is, of course, very rough; the most that can be asserted is that  $\gamma'$  is a positive quantity of the same order of magnitude as, and

probably somewhat less than  $\gamma$ . The motion is only just stable with this load, however, and can be made unstable by a very small reduction of  $\beta_0$ , and I think the figures are a proof that there is an element of instability other than a possible negative value of  $\gamma'$ .

To get an approximation to the absolute value of  $\gamma$ , we note that

$$\delta^2 = \frac{A^2(L + \kappa)p^2}{2M\{(L + \kappa)^2p^2 + \rho^2\}}, \text{ nearly.}$$

Hence

$$4Mp^2 = \frac{A^2p^2(L + \kappa)p^2}{\{(L + \kappa)^2p^2 + \rho^2\}\delta^2} = \frac{4 \times (70)^2 \times 3.5 \times 314}{13.6 \times (17)^2} = 5500 \text{ nearly,}$$

and

$$\frac{1}{\gamma} = \frac{4Mp^2}{960} = \text{about } 5.7 \text{ secs.,}$$

which is the sort of magnitude one would expect from the rate of development of the oscillations when the motor is unloaded and  $\gamma'$  is small or slightly negative.

*Note Added June 28th, 1903.*

It is useful to consider the effect of increasing the dimensions of the machine on the results here obtained. Suppose that the linear dimensions of every part except the field coils are increased  $n$ -fold, that the speed remains the same. Then :

|          |         |             |
|----------|---------|-------------|
| A        | becomes | $n^2A$ ,    |
| $\rho$   | „       | $\rho/n$ ,  |
| L        | „       | $nL$ ,      |
| $\kappa$ | „       | $n\kappa$ , |
| M        | „       | $n^5M$ .    |

The rated output is multiplied by between  $n^3$  and  $n^4$ . To get the same magnetisation we require  $n$ -times the ampère turns in the field-coils. Hence if the number of turns in the field-coils and the current density be kept the same, we require  $n$ -times the section of wire, and the wire is  $n$ -times as long. Since all the other linear dimensions of the coils and of the magnetic circuit are increased  $n$ -fold, it readily follows that  $\mu$  (if the magnets are completely laminated and there are no amortisseur coils) is increased  $n$ -fold.

Taking these values, we find that

$$\delta \left[ = \sqrt{\left( \frac{A^2}{2M(L + \kappa)} \right)} \right] \text{ becomes } \frac{\delta}{n},$$

$$\gamma \left( = \frac{\rho A^2}{4M(L + \kappa)^2 p^2} \right) \quad \quad \quad \text{„} \quad \quad \frac{\gamma}{n^4}.$$



Hence  $\mu\delta$  is unaltered and the damping term

$$\gamma' = \frac{\kappa\mu\beta_0^2}{4M \left\{ \mu^2\delta^2 + \left(1 + \frac{\kappa}{L}\right)^2 \right\}}$$

becomes  $n\gamma'$ , assuming that corresponding values of the current are as  $n^2:1$ . As a fact corresponding values of the current (that is, values which are the same fraction of the maximum rated output) are in a somewhat less ratio than  $n^2:1$ , so that  $\gamma'$  increases but very little with  $n$ .

It appears, therefore, that the coefficient of instability decreases very rapidly with increasing size, while the damping coefficient  $\gamma'$  increases somewhat. At the same time, owing to the rapid decrease of  $\rho/L\rho$ , the critical value of the load at which  $\gamma'$  becomes negative, rapidly becomes smaller in relation to the output of the machine. It may be inferred that a machine similar to that experimented with and but very little larger, would run stably at practically all loads.

In actual practice the dimensions of a pair of adjacent poles and of a corresponding piece of armature in a section perpendicular to the axis are rarely more than two or three times those on the machine here experimented with even in big alternators; the increased output is obtained by increasing the number of poles and by increasing the length of the machine. The number of poles and the length of the machine, provided the peripheral speed remains the same, have but little effect on the quantities  $\gamma$ ,  $\gamma'$  and  $\delta$ . In other words the performance of a machine as regards hunting is determined almost wholly by the form and dimensions, in a section perpendicular to the axis, of a pair of poles and the corresponding bit of armature. The weight of a corresponding bit of fly-wheel (if there is one) must, of course, be added to that of the bit of armature. Thus it is quite conceivable that machines of large size, but with small armature reaction and self-induction, might be constructed in which the quantity  $\gamma$  would be important and the running unstable, at any rate at low loads, though if the magnetic circuit of the machine were similar to that of the one experimented on (in which the self-induction and armature reaction are pretty high), and of double its linear dimensions or more, the motion would undoubtedly be stable.

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"The Spectra of Metallic Arcs in an Exhausted Globe." By  
A. FOWLER, A.R.C.Sc., F.R.A.S., and HOWARD PAYN, F.R.A.S.  
Communicated by Sir NORMAN LOCKYER, K.C.B., LL.D.,  
F.R.S. Received June 10,—Read June 18, 1903.

## [PLATE 14.]

Working on the supposition that the bands which occur in the arc spectrum of magnesium are due to possible combinations of the metal with gases in the outer part of the arc, we have recently attempted to obtain the line spectrum free from bands by photographing the spectrum when the arc is passed in an exhausted globe. It is found, however, that while the band beginning at  $\lambda$  5007.5 is sometimes greatly reduced in intensity under these conditions, the bands attributed to "magnesium hydride" by Messrs. Liveing and Dewar\* are very strongly developed.

Besides this, the characteristic spark, or "enhanced" line at  $\lambda$  4481.3, which is almost invisible in the ordinary arc in air, is one of the strongest lines in the spectrum. Special interest attaches to this line on account of its application to the determination of relative stellar temperatures, based on the variations in the spectrum of magnesium under different conditions, which were first systematically investigated in relation to temperature by Sir Norman Lockyer in 1879.†

The occurrence of the line 4481 in the arc spectrum under special conditions was first recorded by Liveing and Dewar in 1888‡, and has since been investigated by other observers. Crew§ found that the line appeared in the spectrum of magnesium when the arc was surrounded by an atmosphere of hydrogen, and a little later Porter|| found among other results, that a similar effect was produced by oxygen. Experiments by Sir Norman Lockyer and the writers have confirmed these observations.

More recently, Hartmann and Eberhard¶ have observed that enhanced lines appear in the arc spectra of magnesium, zinc, and cadmium when the arc is made to pass in water. The spectra obtained in this manner are stated to be almost identical with those obtained when the arc is passed in a current of hydrogen, and the opinion is expressed that the change is produced by hydrogen released by electrolysis around the electrodes in water. Hartmann has since found

\* 'Roy. Soc. Proc.,' vol. 32, p. 196.

† 'Roy. Soc. Proc.,' vol. 30, p. 29; also 'Chemistry of the Sun,' p. 242; and 'Inorganic Evolution,' p. 75.

‡ 'Roy. Soc. Proc.,' vol. 44, p. 241.

§ 'Astrophys. Journ.,' vol. 12, p. 167, 1900.

|| 'Astrophys. Journ.,' vol. 15, p. 281, 1902.

¶ 'Sitz. der Preuss. Akad. der Wiss.,' 1903, IV, p. 40; 'Astrophys. Journ.,' vol. 17, p. 229.

that the magnesium line 4481 becomes stronger in the spectrum of the metallic arc in air as the current strength is lessened.\*

The occurrence of enhanced lines in the spectrum of the arc at reduced pressure, however, does not appear to have been previously recorded, and it may, therefore, be useful to state briefly the results which have been obtained.

### *Method of Experiment.*

The experiments were conveniently made by enclosing the arc in a glass globe of about a litre capacity having two necks and an outlet by which connection was made with a Töpler pump. Short rods of the metal to be experimented upon were attached to brass rods passed through the two necks and made air-tight with a packing of rubber tube and Chatterton's compound.

The pole pieces were put nearly in contact, so that a slight pressure on one of them sufficed to strike the arc. With this arrangement the arc can only be observed for a comparatively short time owing to the burning away of the poles, and the experiment is also interrupted by the formation of a deposit on the interior of the globe. Still it is usually possible to take two or three photographs in each setting up of the apparatus. Ordinary commercial metals cast into rods a quarter of an inch in diameter were used.

[*Note added July 16.*—In each case the exhaustion was carried as far as the nature of the apparatus would permit. The pressure on starting the arc was from 1 to 2 mm.

The current was obtained from a 100-volt circuit, and in a repetition of the experiment with magnesium poles, measurements have shown that the current strength usually employed was 7 ampères for the arc in air and 8 for the arc under reduced pressure.]

### *Magnesium.*

The well-known triplets beginning at 5183·84 ( $b_1$ ) and 3838·44 are apparently little affected when the globe is exhausted, but the lines 5528·75, 4703·33, 4352·18, 4167·81, 4058·45, and 3987·08, which form a regular series,† are usually sharper than in the ordinary arc, and in some photographs four additional members of the series are seen (approximate wave-lengths 3938, 3904, 3879, 3860).

The band 5007·5, as already remarked, is generally reduced in intensity, while the "hydride" bands, beginning at 5618, 5210, 4849,

\* 'Sitz. der Preuss. Akad. der Wiss.' 1903, XII, p. 234; 'Astrophysical Journ.,' vol. 17, p. 270.

† Rydberg, 'Öfversigt af Kongl. Vet. Akad. Forhandl.,' 1893, Stockholm.

appear with great intensity. Flutings of nitrogen also appear in some of the photographs.

The enhanced line 4481·3 is of about the same intensity as  $b_1$ , and stronger than the lines 4703 and 4352. It is also notably sharp as compared with its usually hazy appearance in the spark spectrum of the metal.

Two conspicuous pairs of sharply defined lines which appear at approximate wave-lengths 4385, 4391 and 4428, 4434 cannot be traced to any known impurities, and a comparison with the spark spectrum leaves no doubt that they are true enhanced lines of magnesium. They are very ill-defined in the ordinary spark, but are distinctly visible as double lines in a photograph of the spark spectrum when a small amount of self-induction is introduced into the secondary circuit, though disappearing when the self-induction is increased. The line at 4391 is apparently identical with the enhanced line recorded by Sir Norman Lockyer\* at 4395. Porter† has observed lines at approximate wave-lengths 4390, 4430 and 4434 in the spectrum of the magnesium arc in an atmosphere of ammonia or oxygen which probably correspond with three of the above four lines, but states that he has not succeeded in identifying them.

Another spark line of small intensity recorded by Thalèn and others at  $\lambda$  4587 does not appear in the photographs of the spectrum of the arc in the exhausted globe, but Porter finds it among the lines of the magnesium arc in ammonia.

It is important to note also that in some of the photographs there is a distinct line coincident with the F ( $H_\beta$ ) line of hydrogen.

[*Note added July 16.*—The identification of this line has been confirmed by visual observations showing the presence of both  $H_\beta$  and  $H_\alpha$ .]

Another point of importance, in considerations as to temperature conditions, is that the flutings and enhanced lines appear to originate in different parts of the arc.

### *Zinc.*

The strong triplet of lines at  $\lambda\lambda$  4810·71, 4722·26, 4680·38, and the adjacent line 4630·06, appear as strong lines, but are generally sharper than the corresponding lines in the spectrum of the arc in air at atmospheric pressure. Most of the other lines in the region D to K disappear altogether or are greatly reduced in intensity.

The well-known spark lines 4912·2, 4924·8 (Thalèn's wave-lengths corrected to Rowland's scale) make their appearance with considerable

\* 'Roy. Soc. Proc.,' vol. 61, p. 168.

† 'Astrophys. Journ.,' vol. 15, p. 277.

intensity, though they are less striking than the principal enhanced lines which appear in the case of magnesium (Plate 14).

Strong flutings also appear, the principal one commencing with a sharp head near  $\lambda$  4300 and grading off towards the violet. These are identical with flutings which appear in the spectrum of the arc when zinc poles are surrounded by an atmosphere of hydrogen, and may therefore be provisionally attributed to "zinc hydride." These flutings have also been observed in the zinc arc in hydrogen by Basquin,\* who also "in lieu of a better hypothesis" attributes them to a compound of hydrogen with the metal.

In one experiment the stronger flutings of nitrogen appeared in the spectrum, but they were apparently restricted to the region surrounding one of the poles. The F line of hydrogen also appears in some of the photographs.

As in the case of magnesium, there is evidence that the flutings and enhanced lines do not originate in the same part of the arc.

#### *Cadmium.*

The phenomena are generally similar to those observed in the case of zinc, but some of the features are less marked. The strong triplet  $\lambda\lambda$  5086.06, 4800.09, 4678.37 and the adjacent line 4662.69 are of reduced intensity, but more sharply defined than in the ordinary arc, while most of the other arc lines in the region D to K disappear. The spark lines 5379.3, 5338.6 are certainly present but not conspicuous.

Strong flutings, fading towards the violet, are seen, the principal heads having approximate wave-lengths, 4491 and 4298. Here, again, the flutings are identical with those which appear when the cadmium arc is surrounded by hydrogen, and may therefore be provisionally regarded as originating in "cadmium hydride."

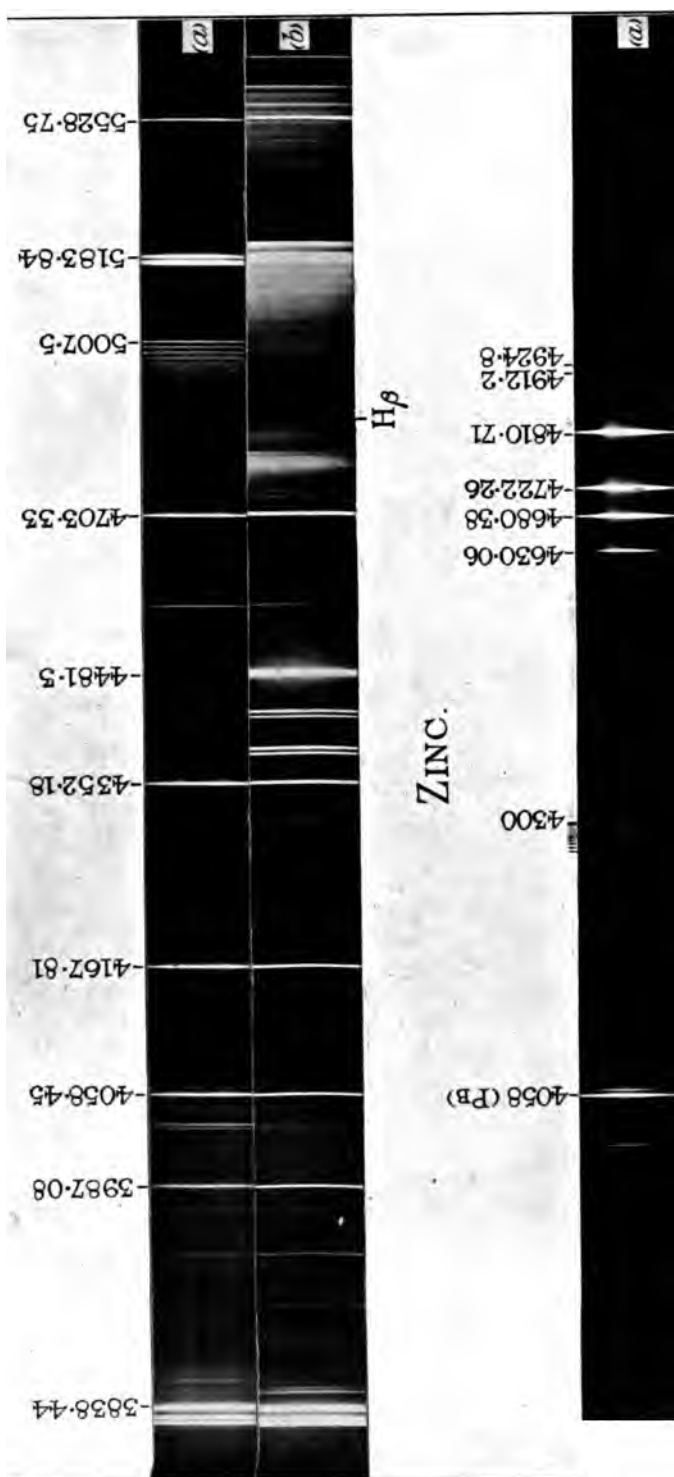
The F line of hydrogen, if present, is too feeble to be shown in the photographs.

#### *Iron.*

It is only after careful examination that the spectrum of an iron arc in an exhausted globe is seen to be materially different from that of the arc in air at atmospheric pressure. Nevertheless, there is no doubt as to the appearance of the principal enhanced lines, among them being 5018.13 and 4584.02.

The F line of hydrogen is not certainly present, but it could not be distinguished from the neighbouring iron line with the dispersion employed unless comparatively strong.

\* 'Astrophys. Journ.', vol. 14, p. 10, 1901.





*General Conclusion.*

So far as they go, the experiments seem to suggest that the modifications of the arc spectra in an exhausted globe may be due to the presence of hydrogen liberated from the heated poles. It has already been pointed out that one of the effects of a hydrogen atmosphere on a metallic arc is to introduce enhanced lines into the spectrum, and the presence of hydrogen under the new conditions of experiment is indicated in the case of magnesium and zinc by the appearance of the  $H_{\beta}$  line, and in magnesium, zinc, and cadmium by flutings which are known to appear in the presence of hydrogen.

It is well known that hydrogen is occluded by many metals, and experiments made to determine the relative amounts of the gas given off on heating *in vacuo* show that the amounts are roughly proportional to the relative strengths of the enhanced lines appearing when the arc passes in the exhausted globe; that is, magnesium and zinc gave off the greatest quantities of the gas, cadmium the least, and iron an intermediate amount. The apparent absence of the F line in the spectra of cadmium and iron in the exhausted globe may, therefore, be due to its feeble intensity on account of the smaller quantity of gas driven out, while the absence of "hydride" bands in the case of iron may perhaps be explained by supposing that combination of hydrogen with iron does not readily take place.

The exact nature of the action of hydrogen on the arc requires further investigation.

The experiments described in the foregoing paper have been made in Sir Norman Lockyer's laboratory, to whom we desire to express our thanks for the privileges afforded. We also wish to express our thanks to Mr. F. W. Jordan for assistance in carrying out the experiments.

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"The Phenomena of Luminosity and their possible Correlation with Radio-Activity." By HENRY E. ARMSTRONG, F.R.S., and T. MARTIN LOWRY, D.Sc. Received June 11,—Read June 18, 1903.

[Dynamic isomerism in relation to luminous phenomena.]

The possibility of regarding *luminous manifestations* generally—including radio-activity—as the outcome of oscillatory changes in molecular structure has already been pointed out by one of us in a communication made to the Society more than a year ago,\* in which the kind of change contemplated was exemplified by reference to the case of nitrocamphor. As the phenomena of radio-activity are exciting so much interest, it appears desirable to enter somewhat more fully into an explanation of the argument underlying this conception of the origin of luminous appearances.

In the note referred to, it was suggested that *tribo-luminescent* substances, i.e., substances which become luminous at the moment of crushing, might conceivably, at the same time, manifest radio-activity. Sir William Crookes has recently examined saccharin from this point of view, using freshly prepared crystals which one of us had placed at his disposal. We are much indebted to him for the following account of his observations:—

"The crystals of saccharin, when broken in the dark, gave off flashes of light.

(1) A sensitive photographic film was covered with a sheet of aluminium foil, 0·04 mm. thick and some crystals were broken on the foil. On development no darkening was seen.

(2) A similar experiment, in which black paper was used instead of aluminium foil, also gave negative results.

(3) Some crystals of saccharin were broken close to the sensitive surface of a photographic film. The flashes of light could be seen through the film. On development some spots were seen on the film which were caused probably by the light given off.

(4) A crystal was broken near the surface of a barium platino-cyanide screen. The screen glowed at the moment of the flash from the crystal.

(5) A crystal of saccharin was put on a hard surface and a screen of barium platino-cyanide was laid face upwards on it. By means of pressure on the screen the crystal beneath was crushed, when a

\* Henry E. Armstrong: "The Conditions Determinative of Chemical Change and of Electrical Conduction in Gases and on the Phenomena of Luminosity." 'Roy. Soc. Proc.,' 1902, vol. 70, p. 99.

flash of luminosity was seen to cover the screen over the place where the crystal was broken.

(6) A screen of hexagonal blende was taken and experiments (4) and (5) were repeated with it. The results were negative, except that I fancied there might be a trace of light when the crystal was broken close to the sensitive surface of the screen."

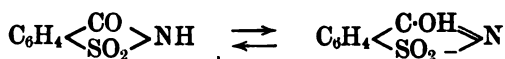
Although it may be argued from experiment (5) that saccharin is radio-active when crushed, we have been unable hitherto to detect any effect on the electrometer. Through the kindness of Dr. Lapworth we have been able also to examine the menthyl phenylformylacetate recently described by him, a substance capable of existing in isodynamic forms, which is not only intensely triboluminescent but gives out most brilliant flashes of light as it separates from solution, its behaviour in this respect being, if possible, even more striking than that of radium in face of a screen of hexagonal blende to which Sir William Crookes has directed attention. As a small quantity of this substance was crystallising out from petroleum spirit, no fewer than ninety-two flashes were observed in broad daylight in the course of ten minutes. Even this substance, however, has not hitherto given positive results when tested by the electrometer.

#### *Triboluminescence.*

We have now to consider the nature of the change involved in the production of the luminous flash, in order that it may be clear why, in our opinion, if radio-activity were observed in such a case, it would have been as the concomitant to chemical change.

There is distinct evidence that the phenomena of triboluminescence may be correlated with the occurrence of the form of isomeric change which attends the passage of a compound into the isodynamic\* form of lower potential. Tschugaeff, who has examined over 500 inorganic and organic compounds,† found that about 25 per cent. of the latter gave a more or less intense flash when crushed; of these a considerable proportion appear to be such as could exist in isodynamic forms. Only about 5 per cent. of the inorganic substances flashed.

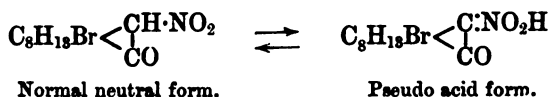
To take the case of saccharin, the two conceivable forms are :



\* This term has been introduced by one of us as being more appropriate than the term tautomeric to connote substances which are apparently almost equipotential—as they so closely simulate one another in behaviour under ordinary circumstances—and are easily interconvertible.

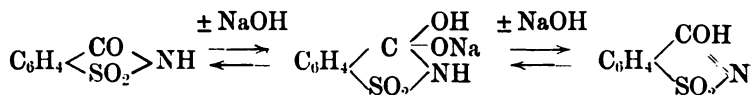
† 'Ber. Deut. Chem. Ges.,' 1901, vol. 34, p. 1820.

Comparable with these are the two isodynamic forms of  $\pi$ - and  $\beta$ -bromonitrocarnphor, for example :



In the solid state, both forms of  $\pi$ -bromonitrocarnphor are stable : when either form is dissolved in a liquid, isomeric change sets in ; sooner or later, it may be only in the course of a few hours or even days, a state of equilibrium is established, about 6 per cent. of the material being present in the pseudo form and 94 per cent. in the normal form.\* The change, however, does not occur spontaneously but is undoubtedly dependent on the presence of a catalyst, as equilibrium is established with great rapidity if a trace of alkali be added ; acids have only a slight, although definite, accelerating effect. In the case of  $\beta$ -bromonitrocarnphor, solutions in benzene of the neutral as well as of the acid form which have been kept during several days without undergoing change, when transferred to another vessel, have rapidly passed to a condition of equilibrium—doubtless because this vessel had been less successfully cleansed than that first used. It can, therefore, scarcely be doubted that the change occurs within a complex system—one which, it is only reasonable to suppose, constitutes an electrolytic circuit. The process is reversed when crystallisation sets in ; if the evaporation of the solvent take place sufficiently slowly, the whole of the material is converted into and crystallises out in the less soluble form ; if, however, evaporation take place rapidly, the isomeric change may lag behind the crystallisation and both forms may separate. In the case of nitrocarnphor, the normal form is the one that separates from the solution ; but in the case of  $\pi$ - and  $\beta$ -bromonitrocarnphor, although the pseudo form is the minor constituent in the solution, being much less soluble than the isomeric form, it is one to separate on crystallisation.

The passage of the one form into the other in the case of saccharin, for example, may be pictured as involving the occurrence of changes such as are represented in the equation :



Supposing the stable form of lower potential to crystallise out, the crystals, in almost every case, would contain a minute and variable amount of the isodynamic form entangled, as it were, in the mass. In

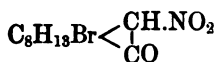
\* Compare Lowry, 'Chem. Soc. Trans.,' 1898, p. 966 ; 'Chem. Soc. Proc.,' 1903, p. 129.

the solid, reversion to the stable form would take place very slowly. Presumably, however, sudden crushing of the crystals would afford opportunity for the change to take place and for the sudden *liberation of energy*—hence the momentary flash.

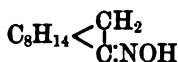
In support of this view we have the fact:—

1. That the phenomenon of triboluminescence occurs irregularly in the case of saccharin: being sometimes shown by one crop of crystals and not by another, the highly purified substance—Professor Pope informs us—being inactive.

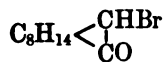
2. That whereas the phenomenon is observed in the cases of three derivatives of camphor which are obviously capable of existing in isodynamic forms,\* viz.,



$\pi$ -Bromonitrocamphor.

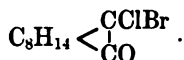


Camphoroxime.



$\alpha$ -Bromocamphor.

it is not seen in the case of camphor derivatives which, although otherwise similar, cannot exist in isodynamic forms, *e.g.*,  $\alpha$ -chloro- $\alpha$ -bromocamphor:



It is not, at present, necessary to assume that the phenomena are limited to cases of isomeric change; obviously, changes such as those above considered, may be regarded broadly as dissociative or reversible changes; and from this point of view, it is sufficient to regard the phenomena as the outcome of a loss of potential consequent on the passage from an unstable to a stable system. Thus, if Tschugaeff's statement that a salt such as aniline hydrochloride is triboluminescent be confirmed by observation with the highly purified substance, it will be justifiable to assume that when it is crushed the manifestation of luminosity may be due to the re-formation of salt momentarily dissociated by pressure.

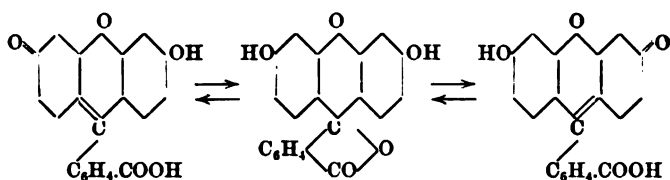
From the point of view here advocated, it would be impossible to construct a condenser from a *pure* dielectric; and if the dielectric of a charged condenser were suddenly smashed under suitable conditions, it might exhibit the phenomenon of triboluminescence and perhaps radio-activity.

#### *Fluorescence.*

It was originally suggested by one of us, in discussing the origin of visible colour, that fluorescence is the "beginning of colour." Subsequently, Dr. J. T. Hewitt, in a paper on the relation between

\* Nitrocamphor does not flash when crushed; perhaps this is because of its texture. It may be that the effect will be observed at lower temperatures.

constitution and fluorescence, published early in 1900,\* took the important step of associating the appearance of fluorescence not with the mere occurrence of the quinoid type of structure which one of us has long contended is characteristic of visibly coloured substance, but with the continued *development* of such a structure—in other words, he has regarded it as the outcome of oscillatory changes in the course of which a non-quinonoid compound undergoes conversion into the isodynamic quinonoid compound,† for example, in the manner represented by the formulæ which picture the changes undergone by fluorescein :



According to Hewitt, "all the molecules will be undergoing tautomeric change continuously and frequently, and energy absorbed when the molecules have one configuration will be, to an appreciable extent, emitted when they correspond to the other configuration. It is practically certain that the vibration frequency of fluorescein is different in the two states, and hence every opportunity is offered for energy of a rapid vibration frequency to be largely transformed into energy of greater wave-length."

Hewitt obviously does not regard fluorescence as a "flash phenomenon" but as a form of colour, as it were.

While agreeing with Hewitt, that the origin of the effect is to be sought in the occurrence of reversible changes involving the production of dynamic isomerides, we think that fluorescence is to be regarded as something apart from colour, which, more often than not, is superposed upon colour. Colour appears to be dependent on selective absorption and scarcely to involve any *return* of the absorbed energy as light. The character of the colour effect in fluorescence is quite distinctive; it is not only remarkable on account of its intensity, but there is in it an indefinable qualitative difference which seems to separate it from ordinary colour. If regarded as a "flash phenomenon" this difficulty disappears.

Hewitt appears to regard fluorescence as the outcome of mere

\* 'Chem. Soc. Proc.,' 1900, vol. 16, p. 3; 'Zeit. Phys. Chem.,' 1900, vol. 34, p. 1.

† In this connection, attention may be called to the following passage which occurs in a note by one of us on fluorescence in quinine salts ('Chem. Soc. Trans.,' 1892, p. 790):—"It is well known that the oxy-salts of quinine are alone fluorescent, salts like the chlorhydride not being so; it is conceivable that this is due to the inferior stability of the former in solution and that, owing to the occurrence of dissociation, a condition is engendered favouring the passage by dynamic change from the non-fluorescent centric to the fluorescent ethenoid condition."

intramolecular wobble. To us it seems likely that the change is conditioned by a catalyst and that it occurs within a complex electrolytic circuit. From this point of view the fluorescence of uranium glass is noteworthy, as showing that changes in molecular structure may go on in a solid viscous medium. It will be desirable to ascertain whether such glass is fluorescent at low temperatures at which it ceases to be viscous.

### *Phosphorescence.*

The phenomena of phosphorescence need to be considered with reference both to cases in which the manifestation attends oxidative or other kinds of chemical change (the glow of phosphorus, the glow-worm, phosphorescent bacteria) and to those in which it is induced by exposure to light (luminous sulphides). The former might well almost be regarded as cases of fluorescence, as a continual supply of energy is derived from the continued occurrence of a chemical change involving loss of energy. With regard to the latter, it would seem that it is not a property of pure substances. Thus it is known that the production of sulphides which can be rendered luminous by exposure to light is dependent on certain special conditions being fulfilled, that, for example, barium sulphide, which is not sensitive *per se*, becomes highly so when it is associated with a minute proportion of bismuth.\*

The phosphorescent medium may be pictured as a complex system capable of undergoing "electrolytic" deformation under the influence of light of high refrangibility: as the changes thus induced are reversed, the energy stored up during insolation becomes liberated and the persistence of the effect is but a consequence of the fact that the change takes place under restraint, in a viscous medium.

Dewar's remarkable observations on phosphorescence at low temperatures clearly foreshadow the conclusion that the property is to be correlated with structure. The two most remarkable classes of substances, he states, are the Platinocyanides amongst inorganic compounds and the Ketonic compounds amongst organic. But these latter are precisely those which are most prone to undergo conversion into isodynamic forms. It is very noteworthy that, according to Dewar, "water when pure is only feebly phosphorescent but remarkably so when impure."

\* L. E. O. de Visser, 'Rec. Trav. Chim.,' 1901, vol. 20, p. 435; 1903, vol. 22, p. 133. In the case of calcium sulphide, the maximum effect is produced when about 1 atom of bismuth is present to 50,000 of calcium. According to the later paper, bismuth alone does not confer the property, but the presence of a sodium salt in addition makes the mixture sensitive.

*Radio-Activity.*

Pursuing the argument a stage further, it appears to us justifiable to regard the activity of radium tentatively as but an exaggerated form of fluorescence in which radiations unnoticed by substances generally—capable of penetrating substances generally—become absorbed and rendered obvious. Such an explanation, from the chemist's point of view, is at least as rational as one which assumes that nature has endowed radium alone of all the elements with incurable suicidal monomania, especially as exothermic changes, when once started, have a tendency to occur rapidly, if not explosively.

There seems to be no good reason for assuming that in fluorescent and other ordinary substances we possess screens capable of arresting rays of every conceivable kind; it may well be that our knowledge of solar radiations is not yet complete; that radium should be more powerful than other substances is not surprising seeing that of all the elements known to us, it perhaps has the highest atomic weight. It is also worth noting that radium stands in close relation to the elements which afford luminous sulphides.

With regard to "Thorium and Thorium X," the facts, as stated by Rutherford and Soddy, do not seem to be incompatible with the view that these are but isodynamic forms of thorium or their equivalent, their behaviour being very similar to that of the isodynamic forms of nitrocamphor, the rate of decay and recovery of activity proceeding according to a simple logarithmic law just as does the conversion of one form into the other in the case of nitrocamphor. In any case, it appears desirable to approach the problem from this point of view and to investigate the phenomena far more thoroughly on the chemical side.

Finally, it may be pointed out that the properties discussed in this note are common to not a few substances. Uranium nitrate is not only radio-active but triboluminescent, fluorescent and phosphorescent at low temperatures; and as Dewar has shown in a recent Royal Institution lecture, it becomes highly electrified when cooled. Platinocyanides also are triboluminescent, fluorescent and phosphorescent at low temperatures. That the several manifestations all have their origin in the formation and decay of isodynamic or equivalent systems is therefore by no means improbable.

Whatever the ultimate value of the considerations advanced in this note, they at least serve to show that much may be learnt by further study of the extent to which luminous phenomena generally are to be correlated with structure and structural changes.

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“Radiation in the Solar System: its Effect on Temperature and its Pressure on Small Bodies.” By J. H. POYNTING, Sc.D., F.R.S., Professor of Physics in the University of Birmingham.  
Received June 16,—Read June 18, 1903.

(Abstract.)

PART I.—*Temperature.*

We can calculate an upper limit to the temperatures of fully absorbing or “black” surfaces receiving their heat from the sun, and on certain assumptions we can find the temperatures of planetary surfaces, if we accept the fourth power law of radiation, since we know approximately the solar constant, that is, the rate of reception of heat from the sun, and the radiation constant, that is, the energy radiated at  $1^\circ$  abs. by a fully radiating surface.\*

The effective temperature of space calculated from the very uncertain data at our command is of the order  $10^\circ$  abs. Bodies in interplanetary space and at a much higher temperature may, therefore, be regarded as being practically in a zero temperature enclosure except in so far as they receive heat from the sun.

The first case considered is that of an ideal earth, more or less resembling the real earth, and it is shown that the temperature of its surface is, on the average,  $325^\circ$ ,  $302^\circ$ , or  $290^\circ$  abs. according as we take for the solar constant Ångström’s value 4 cal./min., Langley’s value 3 cal./min. or a value deduced from Rosetti’s work 2.5 cal./min. The lowest value found,  $290^\circ$  abs., is very near the average temperature of the earth’s surface, which may be taken as  $289^\circ$  abs. As the earth’s effective temperature must, if anything, be below this, and cannot differ much from that of the ideal planet, Rosetti’s value for the solar constant, 2.5 cal./min. or  $0.175 \times 10^7$  ergs/sec., is probably nearest to the true value and is therefore used in the following calculations.

The preceding calculations may be turned the other way. It is shown that, on certain assumptions, the effective temperature of the sun is 21.5 times that of the ideal earth. If we consider that the real earth with a temperature  $289^\circ$  abs. sufficiently resembles the ideal, we get a solar temperature  $21.5 \times 289 = 6200^\circ$  abs.

The upper limit to the temperature of the surface of the moon is determined and is shown to be  $412^\circ$  abs. when no heat is conducted inwards. But Langley finds that the actual temperature is not much

\* W. Wien (‘Cong. Int. de Physique,’ 1900, vol. 2, p. 30) has pointed out that Stefan’s law enables us to calculate the temperatures of celestial bodies which receive their light from the sun, by equating the energy which they radiate to the energy which they receive from the sun, and remarks that the temperature of Neptune should be below  $-200^\circ$  C.



above the freezing point on the average. This leads us to the conclusion that it is not higher than four-fifths the highest possible value, the reduction being due to inward conduction.

The temperature of a small body, dimensions of the order of 1 cm. or less, but still so large that it absorbs radiation, is shown to be nearly uniform, and at the distance of the earth from the sun about  $300^{\circ}$  abs.

Under otherwise similar conditions temperatures must vary inversely as the square root of the distance from the sun. Thus Mars, if an earth-like planet, has a temperature nowhere above  $253^{\circ}$  abs., and if a moon-like planet, the upper limit to the temperature of the hottest part is about  $270^{\circ}$ .

#### PART II.—*Radiation Pressure.*

The ratio of radiation pressure due to sunlight to solar gravitation increases, as is well known, as the receiving body diminishes in size. But if the radiating body also diminishes in size this ratio increases. It is shown that if two equal and fully radiating spheres of the temperature and density of the sun are radiating to each other in a zero enclosure, at a distance large compared with their radii, then the radiation push balances the gravitation pull when the radius of each is 335 metres. If the temperature of two equal bodies is  $300^{\circ}$  abs. and their density 1, the radius for a balance between the two forces is 19.62 cm. If the density is that of the earth, 5.5, the balance occurs with a radius 3.4 cm. If the temperatures of the two are different, the radiation pressures are different and it is possible to imagine two bodies, which will both tend to move in the same direction, one chasing the other, under the combined action of radiation and gravitation.

The effect of Döpler's principle will be to limit the velocity attained in such a chase. The Döpler effect on a moving radiator is then examined and an expression is found for the increase in pressure on the front, and the decrease in pressure on the back of a radiating sphere of uniform temperature moving through a medium at rest. It is proportional to the velocity at a given temperature. The equation to the orbit of such a body moving round the sun is found, and it is shown that meteoric dust within the orbit of the earth will be swept into the sun in a time comparable with historical times, while bodies of the order of 1 cm. radius will be drawn in in a time comparable with geological periods.

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"The Theory of Symmetrical Optical Objectives." By S. D. CHALMERS, B.A. (Cantab.), M.A. (Sydney), St. John's College, Cambridge. Communicated by Professor LARMOR, Sec. R.S. Received and read June 18, 1903.

This paper deals with the relations between the aberrations of a lens system, used with a front stop, and those of the compound system formed by two such systems disposed symmetrically with respect to the stop. The method of Hamilton's characteristic function is used as adapted by Maxwell, the notation employed and the expressions for aberrations of any system being those given by Thiessen.\*

The optical length between the points  $(x_1, y_1, z_1)$ ,  $(x_2, y_2, z_2)$  in the medium  $n_{12}$  is  $n_{12} \{ (x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2 \}^{\frac{1}{2}}$ ; which is expressible in terms of  $x_1, x_2, y_1, y_2$  when the points lie on the surfaces  $z_1 = f_1(x, y)$  and  $z_2 = f_2(x, y)$ .

If these be surfaces of revolution about the axis of  $z$ , their equations may be written  $z = a_1 + b_1\rho_1^2 + c_1\rho_1^4 + \dots$ , where  $\rho_1^2 \equiv x_1^2 + y_1^2$ , and the characteristic, omitting the constant and writing  $\chi_{12}$  for  $-x_1x_2 - y_1y_2$ , is given by

$$T_{12} \equiv A_{12}\rho_1^2 + B_{12}\rho_2^2 + 2C_{12}\chi_{12} + D_{12}\rho_1^4 + E_{12}\rho_2^4 + 4F_{12}\chi_{12}^2 + 2G_{12}\rho_1^2\rho_2^2 + 4H_{12}\rho_1^2\chi_{12} + 4J_{12}\rho_2^2\chi_{12}$$

to terms of the 4th order in  $x, y$ , where,

$t_{12}$  representing  $a_2 - a_1$ ,

$$A_{12} = n_{12} \left( \frac{1}{2t_{12}} - b_1 \right), \quad B_{12} = n_{12} \left( \frac{1}{2t_{12}} + b_2 \right), \quad C_{12} = n_{12} \left( \frac{1}{2t_{12}} \right),$$

$$D_{12} = -n_{12} \left( \frac{1}{8t_{12}^3} - \frac{b_1}{2t_{12}^2} + c_1 \right), \quad G_{12} = -n_{12} \left( \frac{1}{8t_{12}^3} + \frac{b_2 - b_1}{4t_{12}^2} \right),$$

$$E_{12} = -n_{12} \left( \frac{1}{8t_{12}^3} + \frac{b_2}{2t_{12}^2} - c_2 \right), \quad H_{12} = -n_{12} \left( \frac{1}{8t_{12}^3} - \frac{b_1}{4t_{12}^2} \right),$$

$$F_{12} = -n_{12} \left( \frac{1}{8t_{12}^3} \right), \quad J_{12} = -n_{12} \left( \frac{1}{8t_{12}^3} + \frac{b_2}{4t_{12}^2} \right).$$

..... (I).

The characteristic of the media between (1) and (3) is  $T_{12} + T_{23}$ , where  $x_2, y_2$  are to be eliminated by the relations

$$\frac{\partial}{\partial x_2} (T_{12} + T_{23}) = 0, \quad \frac{\partial}{\partial y_2} (T_{12} + T_{23}) = 0,$$

\* 'Sitzungsberichte der K. Preuss. Akad.,' Berlin, 1890.

giving, when  $B_{12} + A_{23}$  is not zero,

$$T_{13} \equiv A_{13}\rho_1^2 + B_{13}\rho_3^2 + 2C_{13}\chi_{13} + D_{13}\rho_1^4 + E_{13}\rho_3^4 + 4F_{13}\chi_{13}^2 + 2G_{13}\rho_1^2\rho_3^2 + 4H_{13}\rho_1^2\chi_{13} + 4J_{13}\rho_3^2\chi_{13},$$

where

$$A_{13} = A_{12} - \frac{C_{12}^2}{A_{23} + B_{12}}, \quad B_{13} = B_{23} - \frac{C_{23}^2}{A_{23} + B_{12}}, \quad C_{13} = \frac{C_{12} \cdot C_{23}}{A_{23} + B_{12}},$$

$$D_{13} = D_{12} - 4\alpha H_{12} + 2\alpha^2 (G_{12} + 2F_{12}) - 4\alpha^3 J_{12} + \alpha^4 (E_{12} + D_{23}),$$

$$E_{13} = E_{23} - 4\beta J_{23} + 2\beta^2 (G_{23} + 2F_{23}) - 4\beta^3 H_{23} + \beta^4 (E_{12} + D_{23}),$$

$$F_{13} = \alpha^2 F_{23} + \beta^2 F_{12} - 2\alpha^2 \beta H_{23} - 2\alpha \beta^2 J_{12} + \alpha^2 \beta^2 (E_{12} + D_{23}),$$

$$G_{13} = \alpha^2 G_{23} + \beta^2 G_{12} - 2\alpha^2 \beta H_{23} - 2\alpha \beta^2 J_{12} + \alpha^2 \beta^2 (E_{12} + D_{23}),$$

$$H_{13} = \beta H_{12} - \alpha \beta (G_{12} + 2F_{12}) + \alpha^3 H_{23} + 3\alpha^2 \beta J_{12} - \alpha^3 \beta (E_{12} + D_{23}),$$

$$J_{13} = \alpha J_{23} - \alpha \beta (G_{23} + 2F_{23}) + \beta^3 J_{12} + 3\alpha \beta^2 H_{23} - \alpha \beta^3 (E_{12} + D_{23}),$$

..... (II),

in which

$$\alpha = \frac{C_{12}}{A_{23} + B_{12}}, \quad \beta = \frac{C_{23}}{A_{23} + B_{12}}.$$

If, however,  $A_{23} + B_{12}$  is zero,  $(x_3y_3)$  is the Gaussian image of  $(x_1y_1)$  and

$$x_3 = x_1\gamma - x_3(h\rho_3^2 + i\rho_2^2 - 2f\chi_{23}) + x_2(g\rho_3^2 + e\rho_2^2 - 2i\chi_{23}),$$

where  $\gamma = -\frac{C_{12}}{C_{23}},$

$$e = \frac{2}{C_{23}} (E_{12} + D_{23}), \quad h = \frac{2}{C_{23}} \left( \frac{H_{12}}{\gamma^2} + J_{23} \right),$$

$$f = \frac{2}{C_{23}} \left( \frac{F_{12}}{\gamma^2} + F_{23} \right), \quad i = \frac{2}{C_{23}} \left( \frac{J_{12}}{\gamma} + H_{23} \right),$$

$$g = \frac{2}{C_{23}} \left( \frac{G_{12}}{\gamma^2} + G_{23} \right),$$

..... (III).

Thus  $e = 0$  is the condition for the correction of Spherical Aberration,

$i = 0$  „ „ absence of Coma,

$f = 0$  „ „ correction of Astigmatism,

$g = 0$  is the additional condition for Flatness of Field,

$h = 0$  is the condition for no Distortion.

Or if we write  $2F + G \equiv 3K$  and  $2f + g \equiv 3k$ , then

$$k = \frac{2}{C_{23}} \left( \frac{K_{12}}{\gamma^2} + K_{23} \right),$$

and we may use the conditions  $k = 0$  and  $f - g = 0$  together, instead of  $f = 0$  and  $g = 0$ .

Before applying these results to our special problem it is necessary to show that  $f-g=0$  is equivalent to Petzval's condition for Flatness of Field.

From equations (II) it is evident that

$$\frac{F_{13}-G_{13}}{C_{13}^2} = \frac{F_{12}-G_{12}}{C_{12}^2} + \frac{F_{23}-G_{23}}{C_{23}^2} = \Sigma \left( \frac{F-G}{C^2} \right);$$

from (III)

$$f-g = 2 C_{23} \left\{ \frac{F_{12}-G_{12}}{C_{12}^2} + \frac{F_{23}-G_{23}}{C_{23}^2} \right\}.$$

Hence if  $f-g=0$ , we have

$$\Sigma \left( \frac{F-G}{C^2} \right) = 0;$$

that is, using I, we have

$$\Sigma \left\{ \frac{1}{n_{12}} (b_2 - b_1) \right\} = 0, \quad \text{or} \quad \Sigma \left\{ \left( \frac{1}{n_0} - \frac{1}{n_1} \right) \frac{1}{r} \right\} = 0,$$

which is Petzval's form.

It is evident that, if this condition be satisfied for a single system, it is also satisfied for the double symmetrical system and *vice versa*.

#### *Application to the case of Double Symmetrical Objectives.*

Consider the object plane at (0), the image due to the combined system at (3), the stop at (2), and let (1) be the plane symmetrical to (3) with regard to the stop.

Let

$$T_{12} \equiv A_{12}\rho_1^2 + B_{12}\rho_2^2 + 2C_{12}\chi_{12} + D_{12}\rho_1^4 + E_{12}\rho_2^4 + 4F_{12}\chi_{12}^2 + 2G_{12}\rho_1^2\rho_2^2 \\ + 4H_{12}\rho_1^2\chi_{12} + 4J_{12}\rho_2^2\chi_{12},$$

then from symmetry

$$T_{23} \equiv A_{12}\rho_3^2 + B_{12}\rho_2^2 + 2C_{12}\chi_{23} + D_{12}\rho_3^4 + E_{12}\rho_2^4 + 4F_{12}\chi_{23}^2 + 2G_{12}\rho_3^2\rho_2^2 \\ + 4H_{12}\rho_3^2\chi_{23} + 4J_{12}\rho_2^2\chi_{23};$$

let

$$T_{01} \equiv A_{01}\rho_0^2 + \dots,$$

where  $A_{01} = B_{01} = C_{01} = \frac{1}{2t_{01}}$ , and

$$D_{01} = E_{01} = \dots = -\left(\frac{1}{2t_{01}}\right)^3, \text{ assuming } n_{01} = 1.$$

In the complete system

$$\gamma = -\frac{C_{02}}{C_{12}} = -\frac{C_{01}C_{12}}{(A_{12} + B_{01})C_{12}} = -\alpha$$

and

$$\frac{C_{01}}{A_{12}} = \frac{\alpha}{1-\alpha}.$$

$$\begin{aligned} e &= \frac{2}{C_{23}} \{E_{02} + D_{23}\} = \frac{2}{C_{12}} \{E_{02} + E_{12}\} \\ &= \frac{2}{C_{12}} \{2E_{12} - 4\beta J_{12} + 6\beta^2 K_{12} - 4\beta^3 H_{12} + \beta^4 (D_{12} + E_{01})\}, \end{aligned}$$

$$\begin{aligned} h &= \frac{2}{C_{23}} \left\{ \frac{H_{02}}{\gamma^3} + J_{23} \right\} = \frac{2}{C_{12}} \left\{ \frac{-H_{02}}{\alpha^3} + H_{12} \right\} \\ &= \frac{2}{C_{12}\alpha^3} \{ -\beta H_{01} - 3\alpha\beta K_{01} + 3\alpha^2\beta J_{01} - \alpha^3\beta (D_{12} + E_{01}) \} \\ &= \frac{2\beta}{C_{12}} \{ D_{12} + A_{12}^3 \}, \end{aligned}$$

$$\begin{aligned} i &= \frac{2}{C_{23}} \left\{ \frac{J_{01}}{\gamma} + H_{23} \right\} = \frac{2}{C_{12}} \left\{ \frac{-J_{02}}{\alpha} + J_{12} \right\} \\ &= \frac{-2}{C_{12}\alpha} \{ \alpha J_{12} - 3\alpha\beta K_{12} + 3\alpha^2\beta H_{12} + \beta^3 J_{01} - \alpha\beta^3 (D_{12} + E_{01}) - \alpha J_{12} \} \\ &= \frac{2\beta}{C_{12}} \left\{ 3K_{12} - 3\beta H_{12} + \beta^2 D_{12} - \beta^3 \frac{1-\alpha}{\alpha} E_{01} \right\}, \end{aligned}$$

$$\begin{aligned} k &= \frac{2}{C_{23}} \left\{ \frac{K_{02}}{\gamma^2} + K_{23} \right\} = \frac{2}{C_{12}} \left\{ \frac{K_{02}}{\alpha^2} + K_{12} \right\} \\ &= \frac{2}{C_{12}\alpha^2} \{ \beta^2 K_{01} + \alpha^2 K_{12} - 2\alpha^2\beta H_{12} - 2\alpha\beta^2 J_{01} + \alpha^2\beta^2 (D_{12} + E_{01}) + \alpha^2 K_{12} \}, \\ &= \frac{2}{C_{12}} \left\{ 2K_{12} - 2\beta H_{12} + \beta^2 D_{12} + \left( \frac{1-\alpha}{\alpha} \right)^2 E_{01} \right\}. \end{aligned}$$

We have  $h=0$  provided  $D_{12} + A_{12}^3 = 0$ ; but this is the condition that the single lens should be spherically corrected with regard to the centre of the stop.\*

It is further evident that it is impossible to exactly satisfy  $h=0$ ,  $k=0$ , and  $i=0$ , and it is easy to obtain the minimum residual error for a given stop and field.†

\* This result is given by Professor Lummer.

† This was pointed out by H. Bruns, "Das Eikonal," 'Abh. der 2. Klasse K. Sächs. Akad.,' Leipzig, 1895. In both cases the methods employed are essentially different from the above.

When the object is at  $\infty$ , we can express the errors in terms of those of the single system with a front stop.

Let the image due to the single system be at (4), then

$$C_{34} = B_{34} = A_{34} = A_{12}, \text{ since } A_{34} + A_{12} - \frac{C_{12}^2}{B_{12}} = 0, \text{ and } A_{12} - \frac{C_{12}^2}{2B_{12}} = 0,$$

$$\begin{aligned} c_1 = \frac{2}{C_{34}} \{E_{02} + D_{24}\} &= \frac{4}{C_{12}} \left\{ E_{02} + D_{23} - 4 \frac{C_{12}}{2A_{12}} H_{23} + 6 \left( \frac{C_{12}}{2A_{12}} \right)^2 K_{23} \right. \\ &\quad \left. - 4 \left( \frac{C_{12}}{2A_{12}} \right)^3 J_{23} + \left( \frac{C_{12}}{2A_{12}} \right)^4 (E_{23} + D_{34}) \right\} \\ &= \frac{4}{C_{12}} \{E_{12} - 2\beta J_{12} + \frac{3}{2}\beta^2 K_{12} - \frac{1}{2}\beta^3 H_{12} + \frac{1}{16}\beta^4 (D_{12} - A_{12}^3)\}. \end{aligned}$$

Again

$$\begin{aligned} \frac{K_{24}}{C_{24}^2} &= \frac{K_{23}}{C_{23}^2} + \frac{K_{34}}{C_{34}^2} - \frac{2}{2A_{12}} \frac{H_{34}}{C_{34}} - \frac{2}{2A_{12}} \frac{J_{23}}{C_{23}} + \frac{1}{4A_{12}^2} (E_{23} + D_{34}) \\ &= \frac{1}{C_{12}^2} \left\{ K_{12} - \beta H_{12} + \frac{\beta^2}{4} D_{12} - \frac{\beta^2}{4} A_{12}^3 \right\} \end{aligned}$$

therefore

$$k_1 = \frac{2}{C_{24}} \left\{ \frac{K_{02} C_{24}^2}{C_{02}^2} + K_{24} \right\} = \frac{4}{C_{12}} \left\{ K_{12} - \beta H_{12} + \frac{\beta^2}{4} D_{12} - \frac{\beta^2}{4} A_{12}^3 \right\}.$$

When the object is at  $\infty$ ,

$$\begin{aligned} e &= \frac{4}{C_{12}} \left\{ E_{12} - 2\beta J_{12} + 3\beta^2 K_{12} - 2\beta^3 H_{12} + \frac{\beta^4}{2} D_{12} \right\} \\ &= e_1 + 6\beta^2 k_1 + \frac{4\beta^4}{C_{12}} (D_{12} + 7A_{12}^3) \end{aligned}$$

$$h = \frac{2\beta}{C_{12}} (D_{12} + A_{12}^3),$$

$$i = \frac{6\beta}{C_{12}} \left\{ K_{12} - \beta H_{12} + \frac{\beta^2}{3} D_{12} \right\} = \frac{3\beta}{2C_{12}} k_1 + \frac{\beta^2}{2C_{12}} (D_{12} + 3A_{12}^3),$$

$$k = \frac{4}{C_{12}} \left\{ K_{12} - \beta H_{12} + \frac{\beta^2}{2} D_{12} \right\} = k_1 + \frac{\beta^2}{C_{12}} (D_{12} + A_{12}^3).$$

From these expressions it is evident that the whole system will be stigmatically corrected, if one component is so, and the additional condition  $D_{12} + A_{12}^3 = 0$  is satisfied; the latter is the condition that there should be no Distortion in the whole system. It is impossible, under these conditions, to satisfy  $i=0$  exactly; but it may be shown that in symmetrical objectives, whose aperture-ratio and field correspond to those of modern Anastigmats, the combined effect of  $k$  and  $i$  will be least when  $k=0$ . If also  $e_1=0$  then  $e=0$  with sufficient approximation.

Thus with a lens 100 mm. focal length, aperture ratio F. 7, field  $50^\circ$ , the greatest diameter of the image of any point (defect due to  $i$ ) is 0.2 mm. approx. ; that of a point on the axis (defect due to  $e$ ) will be approx. 0.02 mm.

For these values the effect of terms in T of higher order would be appreciable ; but the results justify the practice of correcting a single component—the back one—for astigmatism and spherical aberration, *provided* due attention is paid to the securing of the condition for no distortion.

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“On the Discharge of Electricity from Hot Platinum.” By  
HAROLD A. WILSON, D.Sc., B.A., Fellow of Trinity College,  
Cambridge. Communicated by C. T. R. WILSON, F.R.S.  
Received June 3,—Read June 18, 1903.

(Abstract.)

This paper contains an account of a series of experiments on the discharge of electricity from hot platinum wires. The main object of the investigation was to determine the influence exerted by the nature of the gas in which the wire is immersed. The first part of the paper contains a short account of some of the results obtained by previous investigators. The rest of the paper is divided into the following sections :—

- (1) Description of apparatus, &c.
- (2) The leak in air, nitrogen and water vapour.
- (3) The variation of the negative leak with the temperature.
- (4) The leak in hydrogen.
- (5) The leak from palladium in hydrogen.
- (6) Summary of principal results.
- (7) Conclusion.

The wire used was of pure platinum, and was mounted like the filament of an incandescent lamp, in a glass tube. A platinum cylinder surrounded the wire, and the current from the wire to the cylinder, with various differences of potential between them, was measured with a galvanometer. The wire was heated by passing a current through it, and its temperature was determined from its resistance.

It was found that at low pressures using a wire not specially cleaned a large negative leak could be obtained. This leak, however, was not the same on different occasions with the same wire, nor with different wires at the same temperature. The leak on first heating a wire is very large, but falls off with the time. If the wire is then left cold for some hours the leak is again large on first heating and falls off as before. If *the wire is kept at a constant temperature and the leak measured for*

a long time, irregular variations in the leak occur, especially with a wire which has been much heated.

The wire disintegrates when heated at low pressures and evolves gas. If the pressure is kept constant, by pumping, the apparatus of course soon gets filled with the gas evolved by the wire, which is mostly hydrogen. The leak measured under such circumstances is, therefore, not the leak in air but that in hydrogen, which, as will be shown below, is much larger than that in air, and depends on the amount of hydrogen in the wire. When the wire is first heated hydrogen is gradually driven out of it and so the leak falls off. On standing cold the wire again absorbs some of the hydrogen, and so the leak is larger again when the wire is heated.

Long-continued heating causes the surface of the wire to become covered with a network of deep cracks, and it seems probable that the irregular variations in the leak which sometimes occur are connected with the formation of these cracks.

The sudden opening of a crack exposes a fresh surface of platinum, and may suddenly set free some occluded hydrogen, and so produce a sudden increase in the leak. It appears that the last traces of hydrogen can only be got rid of with the greatest difficulty, and the wires continue to evolve gas when heated in a vacuum for an extraordinarily long time.

In order to measure the leak in pure air, precautions were taken to get rid of the hydrogen. The wire, after being mounted in its tube, was boiled in nitric acid, and then washed with distilled water. It was then heated to a high temperature in air at atmospheric pressure, and then the air was pumped out until the pressure was very low, the wire being kept hot all the time. Air was then let in again, and pumped out, several times. This treatment entirely got rid of all the irregularities in the negative leak, and greatly diminished the evolution of gas by the wire.

Cleaning the wire with nitric acid, and changing the air in this way, was found to diminish the leak to something like one thousandth part of its ordinary value, and very thorough cleaning of the wire with nitric acid diminished the leak to about one part in 250,000.

The presence of traces of phosphorus pentoxide was found to enormously increase the negative leak, and it is known that alkali salts have a similar effect. The results obtained lead to the conclusion that the negative leak is due to the presence of traces of hydrogen, or possibly other substances in the wire. The reasons for believing that the leak is mainly due to hydrogen will be mentioned later.

With a particular wire, treated in the way described, in air, the small remaining negative leak only falls off slowly at a constant temperature, and does not vary in an irregular manner, so that its variation with the pressure and temperature can be measured.



The negative leak in air at constant temperature in general increases with the pressure. This is shown to be due to ionisation of the air produced by the collisions of the negative ions coming from the wire with air molecules. If the P.D. used is small, no ionisation by collisions occurs, and then the negative leak is independent of the pressure at low pressures.

If  $n_a$  ions leave the wire, the number  $n_b$  of ions reaching the cylinder is shown to be given approximately by the formula

$$\log \frac{n_b}{n_a} = \frac{V}{E \log \frac{b}{a}} \left\{ \epsilon^{\frac{-NEpa}{V} \log \frac{b}{a}} - \epsilon^{\frac{-NEpb}{V} \log \frac{b}{a}} \right\}.$$

In this formula

$V$  = potential difference between wire and cylinder,

$b$  = radius of cylinder,

$a$  = radius of wire,

$p$  = gas pressure,

$N$  = maximum number of negative ions produced by one negative ion in going 1 cm. at unit pressure,

$E$  = potential through which a negative ion must fall to enable it to ionise an air molecule.

Professor Townsend has shown that the number  $\alpha$  of negative ions produced by one negative ion in going 1 cm. is given approximately by the formula

$$\alpha = Np\epsilon^{\frac{-NEp}{X}},$$

where  $X$  is the electric intensity. This formula of Townsend's is used in deducing the above expression for  $n_b/n_a$ .

It is shown that  $N$  varies nearly inversely as the absolute temperature of the gas through which the negative ion moves.

The variation of the negative leak with the temperature is investigated theoretically on the assumption that the liberation of negative ions or corpuscles at the surface of the platinum is analogous to the evaporation of a liquid, and the formula

$$x = A \sqrt{\theta} \epsilon^{-Q/2\theta}$$

is obtained.\* In this formula

$x$  = negative leak per sq. cm. of platinum,

$\theta$  = absolute temperature,

$Q$  = energy in gramme calories required to produce 1 gramme molecular weight of ions,

$A$  = a constant.

\* A formula of this type was first used by the author to calculate the energy necessary for the production of ions from the temperature variation of the leak from hot platinum in 1901. See 'Phil. Trans., A, 1901, p. 430.

It is found that this formula accurately represents the variation of the negative leak with the temperature.  $Q$  is found to be 130,000, and it is shown that it cannot vary more than one part in one hundred thousand per degree Centigrade. The value of the constant  $A$  is shown to be diminished by cleaning the wire with nitric acid. With a wire boiled for a few minutes in nitric acid  $A = 7 \times 10^7$ , while with a wire very thoroughly cleaned  $A = 6 \times 10^6$ .

The negative leak in hydrogen was measured and found to be very much greater than in air. At low pressures, using a P.D. too small to produce ionisation by collisions, the current is proportional to the pressure of the hydrogen. The leak from a wire in hydrogen at 0.1 mm. pressure is several thousand times that from a clean wire in air or in a vacuum.

It is shown that the negative leak in hydrogen depends on the amount of hydrogen absorbed by the wire. When the temperature or pressure is suddenly varied, it takes a considerable time for equilibrium to be established between the hydrogen in the wire and that outside, and the leak varies in consequence with the time. The following table gives the negative leaks at  $1400^\circ \text{C.}$  at several pressures in hydrogen.

| Pressure.  | Current per sq. centimetres. |
|------------|------------------------------|
| 133.0 mms. | $1.0 \times 10^{-3}$ ampère. |
| 0.112 „    | $1.2 \times 10^{-5}$ „       |
| 0.0013 „   | $2.0 \times 10^{-7}$ „       |
| 0.0 „      | $1.2 \times 10^{-10}$ „      |

The following table gives the values of the constants  $Q$  and  $A$  found for wires in air and hydrogen at several pressures:—

| Pressure.                                          | $Q$ .   | $A$ .             |
|----------------------------------------------------|---------|-------------------|
| (1) Thoroughly cleaned wire in air or vacuum ..... | 155,000 | $6.0 \times 10^6$ |
| (2) Cleaned wire in air or vacuum .....            | 131,100 | $6.9 \times 10^7$ |
| (3) 0.0013 mm. $\text{H}_2$ .....                  | 120,000 | $10^7$            |
| (4) 0.112 „ $\text{H}_2$ .....                     | 85,900  | $5.3 \times 10^4$ |
| (5) 133.0 „ $\text{H}_2$ .....                     | 36,000  | 0.1               |

If we regard the leak in air, or a vacuum, as due to traces of hydrogen occluded in the wire, then we see from the above table that  $Q$  steadily increases as the amount of hydrogen in the wire diminishes. The constant  $A$ , however, increases with increasing quantity of occluded hydrogen, when very little hydrogen is present, but when the amount of hydrogen is further increased it attains a maximum, and then diminishes. The fact that the negative leak in air at low pressures always falls off with long continued heating, confirms the view that it is due to occluded hydrogen. Treating the wire with nitric acid

enormously diminishes the negative leak, and also, to a large extent, stops the evolution of gas from the wire when it is heated. The nitric acid, of course, oxidises the hydrogen.

O. W. Richardson\* has recently published two papers on the negative leak from hot platinum and other substances. He obtained large negative leaks from platinum, which behaved in the irregular manner which I have described above as occurring when using wires not specially cleaned. The results which I have obtained do not confirm the theoretical conclusions to which he has been led.

The paper also contains the results of measurements of the positive leak in air and hydrogen. The results confirm the view that the positive leak from clean wires is due to ionisation of the gas molecules at the surface of the platinum.

The view put forward in this paper with regard to the negative leak is that it is generally due to the emission of negative ions by hydrogen occluded in the platinum. Other substances, such as phosphorus pentoxide and alkali salts, also give rise to a negative leak when they are present. Air and nitrogen do not appear to produce any negative leak appreciable on a galvanometer.

It is probable that a pure platinum wire heated in a perfect vacuum would not discharge any electricity at all, either positive or negative, to an extent appreciable on a galvanometer.

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\* 'Proc. Camb. Phil. Soc.,' vol. 11, Part IV; 'Roy. Soc. Proc.,' vol. 71, 1903.

"The Properties of the Aluminium-Tin Alloys." By W. CARRICK ANDERSON, M.A., D.Sc., and GEORGE LEAN, B.Sc. Communicated by Professor H. A. MIERS, F.R.S. Received June 16,—Read June 18, 1903. Received in revised form August 8, 1903.

[PLATE 15.]

Aluminium and tin may be melted together in all proportions to give uniform fluid mixtures. The melting cannot be done in the ordinary fireclay or plumbago crucibles, since the admixture of tin appears to increase greatly the power which aluminium has to reduce the silicates of fireclay, the reduced silicon becoming absorbed in the body of the metal. In our earlier experiments on these alloys we learned that, even with careful melting at a temperature not higher than about  $750^{\circ}\text{C}$ ., it was impossible to prevent this rapid reduction of silicon. In a few minutes the alloys became badly contaminated with the metalloid; in one instance as much as 11 per cent., partly crystalline and partly amorphous, was found in the cooled ingot. On this account the metal was in our subsequent experiments invariably melted in small crucibles of baked carbon. These were packed by means of asbestos inside fireclay crucibles of the ordinary Rattersea type. The ingots made in this way were found to be uncontaminated, and contained only traces of silicon and iron from the aluminium employed, which was the best quality Foyers product. The weight of metal used in each experiment was from 10 to 40 grammes.

*Cooling Curve.*

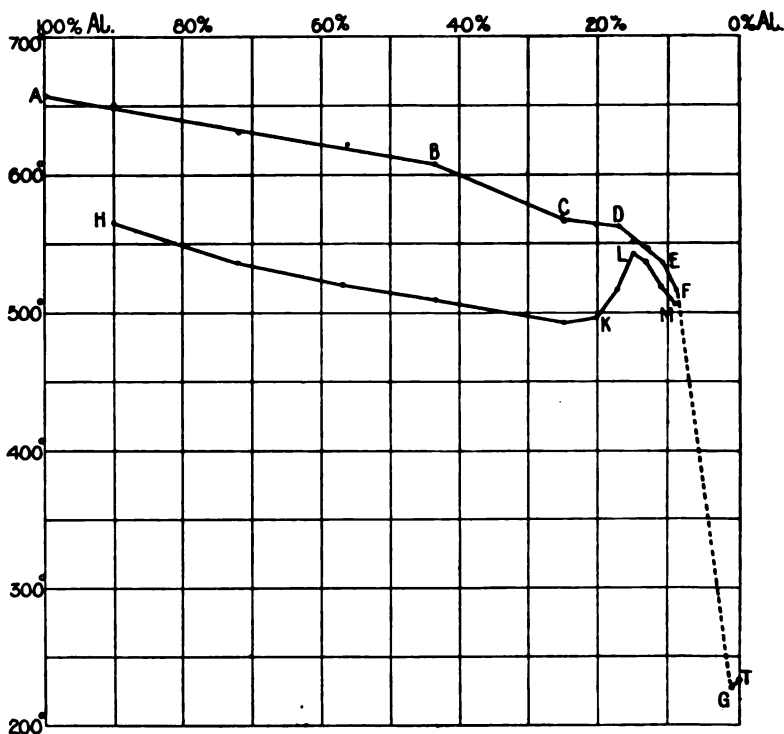
In a preliminary paper on the nature of these alloys, read before the British Association at its Glasgow Meeting in 1901,\* we showed that above the eutectic limit the cooling curve of each alloy always reveals two breaks. The general form of the curve is as we then stated it to be. It has the usual extended form corresponding to the gradual separation of mixed crystals from the solution during cooling, and the first break point is continuously lowered with every increment of tin. The second break, which marks the solidifying point of the eutectic, we were at first inclined to place at  $232^{\circ}$ , or very little below that temperature. More careful working, however, with a larger number of alloys, has enabled us now to place it nearer the figure originally stated by Heycock and Neville,† and rather under it, viz.,  $228^{\circ}$ — $228^{\circ}5$ .

\* 'B. A. Rep.,' 1901, p. 606.

† 'Journ. Chem. Soc.,' 1890, p. 376.

The curve shown in Diagram 1 is obtained by means of a direct-reading Le Chatelier pyrometer. The platinum-rhodium couple was wrapped in a thin covering of asbestos paper, worked into a pulp and dried, and then placed in the thoroughly liquid mixtures of aluminium and tin. The quantities of metal used were the same throughout, and the conditions of experiment were arranged so that the radiation was similar in each case. The curve ABCDEF shows the position

DIAGRAM 1.—Aluminium-Tin Alloys.



of the first halt in the cooling curves of the alloys lying between 100 per cent. aluminium and 9 per cent. aluminium. It is, therefore, the liquidus curve, or freezing-point curve. In each experiment the point of temperature was noted at which the retardation of the fall in temperature ceased and the rate of cooling became once more normal. These temperatures are plotted on the line HKLM, which may, therefore, be regarded as approximating to the points at which active separation of solid matter ceased in each of the alloys. It thus indicates the trend of the solidus curve of the series.

The positions occupied by this first break point in the several alloys

which we examined makes the freezing-point curve connecting these a peculiar one. With the exception of a slight deviation which is apparent at the point B (see curve Diagram 1), it slopes uniformly downwards until about 25 per cent. of aluminium is present (point C on curve). From this point, however, until the percentage of aluminium reaches 17 per cent. (D on curve), the temperature at which the first break occurs remains practically constant. Indeed, when uniformity in the conditions of cooling is maintained, the alloys from 25 per cent. aluminium to 17 per cent. aluminium may be said to begin the separation of solid matter at almost exactly the same temperature, namely  $561^{\circ}\text{C}$ . When the percentages of aluminium are less than 17, the downward trend of the curve is resumed at a more rapid rate than before, with perhaps a slight further deflection at or about the point E in our diagram.

In our experiments the flattening of the curve extended from the alloy having the composition 24.8 per cent. aluminium to that containing 17.43 per cent. Between these limits the first signs of heat evolution appeared at from  $563^{\circ}$  to  $560^{\circ}.5\text{C}$ . A definite compound of the formula  $\text{AlSn}$  would have the composition

|         |                |
|---------|----------------|
| Al..... | 18.5 per cent. |
| Sn..... | 81.5 „         |

Whether the solid matter separating out at the temperature stated has this composition or not, it is at least the case that in that part of the curve to the left of this point the separation is taking place from a solution containing more than one atom of aluminium to each atom of tin; to the right it is taking place from a solution in which atoms of tin preponderate. The homogeneous liquid mixtures, therefore, to the left are solutions of tin in aluminium, those to the right are solutions of aluminium in tin.

A freezing-point curve for these alloys has already been given by H. Gautier.\* His results differ from ours most markedly in this, that in the region CD he finds the separation of solid matter to commence at temperatures higher than is the case in alloys both to the left and right of it. The result is a very pronounced "kink" in the curve, which in our experiments is represented to the extent of only  $1^{\circ}\text{C}$ . in the case of the alloy containing 17.43 per cent. of aluminium. The explanation of the difference is doubtless to be found in the different rates of cooling in the two series of observations. For the sake of comparison we append the figures. The melting point of aluminium is given by Gautier as  $650^{\circ}\text{C}$ .; we have chosen the figure  $655^{\circ}\text{C}$ .

\* 'Comptes Rendus,' vol. 123, 1896, p. 109.

| Gautier.         |                             | Carrick Anderson and Lean. |                             |
|------------------|-----------------------------|----------------------------|-----------------------------|
| Per cent. of Al. | Temp. of separation.<br>°C. | Per cent. of Al.           | Temp. of separation.<br>°C. |
| 100              | 650                         | 100                        | 665                         |
| 83               | 637                         | 90·01                      | 649                         |
| 70               | 622                         | 71·93                      | 630                         |
| 54               | 605                         | 56·63                      | 622                         |
| 27               | 558                         | 43·50                      | 608·5                       |
| 20·5             | 553                         | 24·80                      | 563                         |
| 19·0             | 565                         | 20·20                      | 560                         |
| 15·7             | 580                         | 17·43                      | 561                         |
| 12·5             | 565                         | 15·57                      | 549                         |
| 8·5              | 520                         | 13·31                      | 544                         |
| 7·0              | 500                         | 10·65                      | 537                         |
| 5·5              | 470                         | 8·33                       | 515                         |
| 2·4              | 390                         |                            |                             |
| 1·0              | 328                         |                            |                             |
| 0·05 (0·5 ?)     | 229                         | 0·5                        | 228—228·5                   |
| 0·00             | 232                         | 0·0                        | 232                         |

*Action on Water.*

A remarkable feature of the alloys of the aluminium-tin series, to which we directed attention in our previous paper, is the readiness with which they decompose water with evolution of hydrogen even at ordinary temperatures. The phenomenon is exhibited by every one of the long series of alloys we have prepared, and in all cases the action is greatly intensified by warming the water. In consequence of this action, polished plates left in even slightly damp air become in a few days strongly pitted, and when the phenomenon was mentioned by one of us to the late Sir W. Roberts-Austen, he recalled that certain alloys of these metals, which had been prepared at one time in the Mint and laid aside, were found after a period to have crumbled to powder. We have not noticed the effect so fully developed in any of our specimens, but some which have been for two years in loosely-corked tubes are now becoming swollen and distorted.

In the paper already quoted we stated that we had not then been able to obtain any concordant results for the evolution of hydrogen in the case of the different alloys that might show a connection between the hydrogen given off and the aluminium contained in the alloy. We experimented at the time on alloys cast in chilled moulds, and the same annealed for several hours at various temperatures in the region just below redness. The figures showed, however, that the cast metal *always* yielded more hydrogen than annealed specimens containing the *same* proportion of aluminium. In repeating the experiments the

cast alloys were annealed together for 20 hours at a temperature never varying more than a few degrees from 400° C. Filings were then taken from the specimens, and 0.5 gramme in each case was treated with water. The specimens were placed alongside one another in a water bath kept at 80°—90° C. Some of the experiments were continued for six weeks, but as the evolution of gas in the latter stages is very slight, the later ones were stopped at the end of four weeks, and any small residual evolution neglected.

The results obtained are shown below :—

|                                                           | Composition of alloy.     |                           |                          |                           |                          |                          |
|-----------------------------------------------------------|---------------------------|---------------------------|--------------------------|---------------------------|--------------------------|--------------------------|
|                                                           | 71.98<br>per cent.<br>Al. | 56.68<br>per cent.<br>Al. | 51.8<br>per cent.<br>Al. | 43.73<br>per cent.<br>Al. | 20.2<br>per cent.<br>Al. | 8.33<br>per cent.<br>Al. |
| Gramme atoms<br>of Al. per 100<br>grammes alloy           | 2.65                      | 2.09                      | 1.91                     | 1.614                     | 0.745                    | 0.308                    |
| C.cs. of dry H<br>(at N. T. P.)<br>per gramme of<br>alloy | 356                       | 266                       | 240                      | 184                       | 77                       | 23.3                     |
| C.cs. H per<br>1/100 gramme<br>atom Al.                   | 184                       | 127                       | 125                      | 114                       | 108.7                    | 75.6                     |

Theoretically 1/100 gramme atom of aluminium evolves 334.5 c.c. of hydrogen at N.T.P. (Diagram 2.)

Examination of polished plates of the alloys after corrosion with water shows that the action begins round the edge of the areas of aluminium-rich constituent. Our experiments indeed go to show that the decomposition of water is entirely ascribable to this part of the alloy. We got, it is true, a slight evolution of hydrogen when small pieces of the more fusible, tin-rich constituent expressed from the alloys on heating were placed in water, but, as we shall show later, the composition of this exuded metal is not the same as the eutectic.

The photograph marked "1" illustrates the result of this water action continued for 124 hours at room temperature, on a polished plate containing 65 per cent. aluminium. The aluminium-rich areas have been worn down and corroded, leaving the tin-rich network in relief.

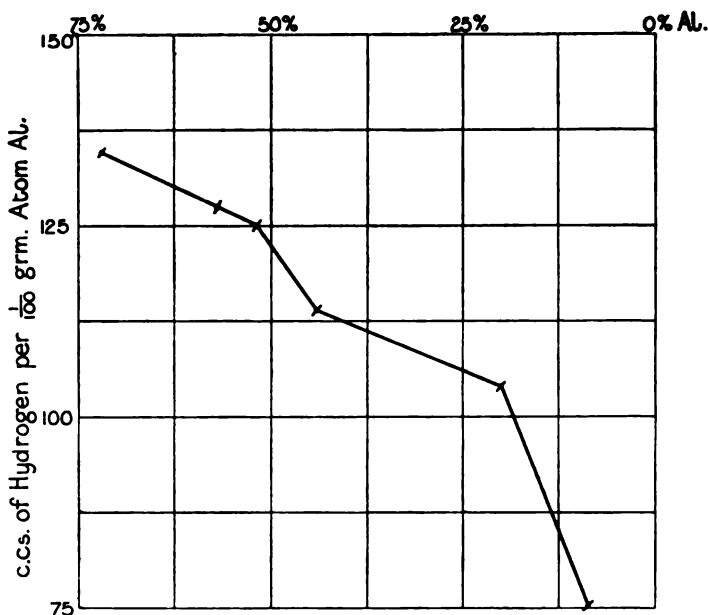
#### *Microscopic Structure.*

The microscopic structure of these alloys is illustrated by the accompanying photographs. The ingots were prepared as already described,



and were cast as before in a chilled mould. One half of the ingot was polished directly and etched for five minutes with a 2-per-cent. solution of caustic potash. The other half was annealed at 400° C. for twenty hours and then treated similarly. The two sets are referred to as the cast and annealed metals. The series examined ranged in composition from 99 per cent. aluminium to 1 per cent. When the percentage of aluminium exceeds that required to saturate the tin, which from our experiments is under 0.5, two constituents are always visible in the solidified alloy. One of these, easily recognisable as

DIAGRAM 2.—Hydrogen Evolutions.



that which solidified first, is abundant in those alloys which are rich in aluminium and decreases in quantity as the percentage of aluminium is lessened. In the cast metals, as illustrated in fig. 2, it is intimately mixed with the second constituent, which is the eutectic, until the aluminium has diminished to about 15 per cent., when it begins to appear in isolated patches in the eutectic. The exact freezing point of this eutectic mixture has been stated by Heycock and Neville to be 228.73° C. Annealing causes the constituent of higher melting point to segregate into patches, and the eutectic becomes then more clearly visible (fig. 3) even in alloys with a high percentage of aluminium. The lowest temperature at which this segregation takes place actively is above 250° and below 300° C. The photographs (figs. 4 and 5)

illustrate the process in the case of the alloy containing 15.42 per cent. of aluminium. No. 4 is a polished area of the cast metal. Heating in a current of dry hydrogen gas causes no marked rearrangement of the constituents at  $216^{\circ}$ — $220^{\circ}$  C., even when continued for 28 hours. The polished surface, however, becomes roughened and presents a warty appearance. Similar results are produced when the experiment is repeated at  $228\frac{1}{2}^{\circ}$ — $232^{\circ}$  C., that is at a temperature just over the melting point of the eutectic. A more marked change is noticeable at  $250^{\circ}$  C., and a tendency to rearrangement is apparent, even after  $9\frac{1}{2}$  hours at the temperature. Finally, when the annealing process is repeated at  $290^{\circ}$ — $300^{\circ}$  for an equal time,  $9\frac{1}{2}$  hours, the repolished and etched surface shows the structure of the alloy to have been profoundly modified thereby, and the appearance under the microscope is now that characteristic of the annealed metal (fig. 5). The round, oval, or sometimes irregular areas of aluminium-rich constituent, show up brilliantly white in the midst of the darker coloured eutectic. The eutectic is soft and on that account somewhat difficult to polish, but, if carefully treated and etched with a 2 per cent. caustic potash solution so as to remove the skin of smeared metal from the surface, it exhibits under a magnification of less than 200 diameters the wavy or striated structure characteristic of eutectic mixtures generally (fig. 6).

The polished and etched plates of these alloys, both cast and annealed, must be examined soon after they are prepared, since the surface rapidly becomes pitted, owing to the action of atmospheric moisture. In the annealed ingots this pitting is seen to be confined to the eutectic areas, and is apparently due to the incomplete segregation of small nuclei of the constituent of higher melting point from the eutectic mixture. Until the percentage of tin in the mixture exceeds that represented by the point C in the curve (Diagram 1), the amount of eutectic visible in the polished plates is not proportional to each addition of tin made. When this point is passed a general proportion between the two may be stated to exist.

Putting together the evidence from the curves, the hydrogen evolutions (Diagram 2) and the microscopic structure, it may be concluded that there is a substance or series of substances present in these alloys marked by the common property of evolving hydrogen from water. The only very marked interruption to the continuity of the curve is in the region CD in the vicinity of an alloy corresponding to the formula  $\text{Al}_2\text{Sn}$ . In the fluid mixtures containing larger percentages of aluminium than 18.5, there are more atoms of aluminium than of tin. From these media there appears to separate at successively lower temperatures solid matter which contains aluminium and tin in the proportions  $\text{Al}_x\text{Sn}_y$ , where the value of  $x$  is at first greater than  $y$ , but is gradually approximating to it. This separation is taking place from a fluid which always contains more atoms of aluminium than of tin. The

final member of this series of solids has the composition  $\text{AlSn}$ , and begins to fall out from a solution of the same composition at  $561^{\circ}\text{C}$ . The line ABCD connects the upper limits at which the separation of solid matter takes place in fluid mixtures containing excess of aluminium atoms. The line HKL marks the lower limit at which in our experiments this separation was active. Within the area ADLKH, the mixture consists of solid, so-called aluminium-rich constituent, by which is to be understood solid containing not less than one atom of aluminium to one atom of tin, along with liquid of approximately the same composition. From mixtures containing about 18.5 per cent. of aluminium and lower proportions than that the last member of the former series  $\text{AlSn}$  is being separated from a fluid medium which contains excess of tin atoms, and the solution is thereby gradually impoverished in respect of aluminium until at the eutectic point,  $228.73^{\circ}$  (Heycock and Neville), it retains only about 0.48 per cent. of that constituent.

The existence of the compound  $\text{AlSn}$  as the terminal member of a series of bodies separating out from the fluid mixtures of aluminium and tin is inferred from the flattening of the liquidus curve at the part CD, in the vicinity of an alloy of this composition, and the small amount of heat liberated in mixtures richer in tin than  $\text{AlSn}$  as indicated by the liquidus and solidus curves approximating closely to one another to the right of that point.

The part of the curve from F to the eutectic point G has not been systematically examined by us, but analyses which we made on the fusible portion of the alloys which is automatically expressed at higher temperatures than the eutectic point, prove that the solvent power of tin for aluminium becomes appreciably greater as the temperature is increased. The liquid metal squeezed out between  $300^{\circ}$  and  $400^{\circ}\text{C}$ . is a solution, when liquid, containing 3 to 4 per cent. of aluminium. The ingots of composition  $\text{Al} = 42.5$  per cent.; 15.4 per cent.; 8.04 per cent., yielded at  $400^{\circ}\text{C}$ . respectively beads of composition

$$\text{Al} = 3.50 \text{ per cent.} : 3.76 : 3.52.$$

The saturated solution of aluminium in tin at  $400^{\circ}$  contains therefore 3.59 per cent. of aluminium, equivalent to 1 part  $\text{AlSn}$  dissolved in 5 parts of the solvent medium having the composition of the eutectic (0.48 per cent.  $\text{Al}$ ). The segregation resulting on very slow cooling of these beads of saturated solution causes the very fluid eutectic residue to be extruded in some cases so as to cover the solid bead with an appendage of fine metallic hairs. The extent of this segregation will be indicated by continuing the line LM in the curve to meet EFG at the eutectic temperature G. The ease with which the compound  $\text{AlSn}$ , aluminium stannide, becomes oxidised, makes it impossible so far to isolate it from the metallic mixture in which it is produced.



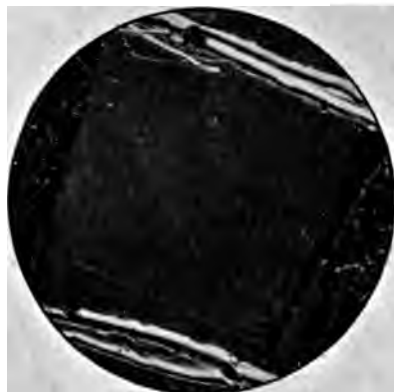
Nº 1.  
%. Annealed & water-  
d for 124 hours.  $\times 19$ .



Nº 2.  
Al. 51.8%. Cast.  $\times 19$ . Oblique Illum.



Nº 3.  
%. Annealed.  $\times 19$ . Oblique Illum.



Nº 4.  
Al. 15.42%. Cast. Annealing Expt  
Oblique Illum.  $\times 19$ .



Nº 5.  
12%. Annealed at 300°C.  
Oblique Illum.  $\times 19$ .



Nº 6.  
Al. 42.5%. Annealed.  $\times 270$ .  
Nacht Prism.

17/10/1919



"Cyanogenesis in Plants. Part III.—On Phaseolunatin, the Cyanogenetic Glucoside of *Phaseolus lunatus*." By WYNDHAM R. DUNSTAN, M.A., F.R.S., Director of the Imperial Institute, South Kensington, and THOMAS A. HENRY, D.Sc., (Lond.). Received June 10,—Read June 18, 1903.

(From the Scientific Department of the Imperial Institute.)

*Phaseolus lunatus* is an annual plant, probably indigenous to South America, but now generally cultivated throughout the tropics, where its edible bean is used as a vegetable. The plant presents much the same appearance as the common French bean, but the flowers are smaller and more numerous, whilst the pods are crescent-shaped and contain only two or three seeds. The latter, according to Cordemoy,\* are violet in the wild state, light brown with violet hues or patches when semi-cultivated, and white in the cultivated state. The beans produced by the wild plant are known in Mauritius as *Pois d'Achery*, those from the semi-cultivated plant as *Pois Amer*, whilst the cultivated product is termed *Pois Adam* or *Pois Portal*, and in English-speaking colonies Lima or Duffin beans.

Whilst the white cultivated beans of *Phaseolus lunatus* have never been known to be poisonous, the coloured beans as well as the plant itself in the semi-wild state have frequently exhibited markedly poisonous properties, and attention is directed to this difference between the white and coloured seeds by Church.†

The semi-cultivated plant grown in Mauritius, where it is utilised as green manure and occasionally as cattle fodder, was examined in 1900 by M. Bonamé, Director of the Agricultural Station at Mauritius, in order to ascertain the cause of its poisonous action. The beans were shown to furnish hydrocyanic acid when crushed and moistened with water.‡ The hydrocyanic acid was found not to exist as such in the plant, but to be in some state of combination, probably in the form of a glucoside which, owing to the simultaneous occurrence in the cells of the plant of a hydrolytic enzyme, underwent hydrolysis, furnishing hydrocyanic acid as one product. No attempt, however, was made by M. Bonamé to isolate the glucoside or enzyme, and only indirect evidence of their existence was recorded on the analogy of the bitter almond. Prussic acid was found to be produced by all parts of the plant, though in greatest quantity by the seeds.

The fresh plant was examined later by van Romburgh,§ who showed

\* 'Flore de la Réunion,' 1895.

† 'Food-grains of India,' p. 155.

‡ 'Rapport Annuel de la Station Agronomique,' 1900, p. 94.

§ 'Annales du Jardin Botanique de Buitenzorg,' Series II, vol. 1, p. 2.

that when crushed, moistened with water and distilled, it furnished a distillate containing hydrocyanic acid and acetone, and this author drew attention to the fact that he had observed the simultaneous production of acetone and hydrocyanic acid in several other plants, notably in *Manihot utilissima*, which furnishes the cassava of the West Indies.

The observations of Bonamé and of van Romburgh suggested to us the advisability of examining *Pois d'Achery* in continuation of the investigation of the chemical origin of the prussic acid of plants, on which we have been engaged for some time. For the material, which is somewhat difficult to procure, we are indebted to M. Bonamé, who, at the instance of the Colonial Office, collected in Mauritius and forwarded to us two large samples of the beans.

#### *Preliminary Observations.*

When a few of the beans are powdered and moistened with cold water, the odour of hydrocyanic acid becomes perceptible in a few minutes. If boiling water is used and the vessel is immediately closed and allowed to cool, no odour of prussic acid is perceptible, and no evidence of its production can be obtained by the application of the usual test to distillates from such preparations. These observations confirm those recorded by Bonamé,\* and indicate that the production of hydrocyanic acid is connected with the action of an enzyme.

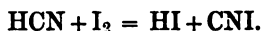
#### *Estimation of the Amount of Hydrocyanic Acid Produced.*

It was found to be impossible to estimate the amount of hydrocyanic acid, obtainable from a weighed quantity of the powdered beans, by soaking the powder in water and subsequent distillation, owing to the continuous frothing over of the liquid. This difficulty, which was experienced by previous workers, was avoided by extracting in a Soxhlet percolator a weighed quantity of the finely ground seeds with 90 per cent. alcohol, distilling off the solvent, hydrolysing the glucoside contained in the residue by distilling with dilute sulphuric acid until hydrocyanic acid no longer appeared in the distillate, and then estimating, by one of the usual methods, the amount of prussic acid thus produced.

Owing to the production of some volatile reducing substance, which was carried over with the hydrocyanic acid in this process, it was difficult to titrate the acid volumetrically by Liebig's method, which we have employed in previous cases, since the end reaction was obscured by the formation of a slight precipitate of reduced silver.

\* *Loc. cit.*

A modification of the method used by Fordos and Gelis\* has, therefore, been used in the present instance. This consists in adding volumetric iodine solution to the liquid containing hydrocyanic acid until the whole of the latter has been converted into cyanogen iodide according to the equation :



The formation of cyanogen iodide is, however, quickly inhibited by the accumulation in the liquid of hydriodic acid. The originators of the process attempted to overcome this difficulty by first rendering alkaline with potash the liquid to be titrated, and then adding water aerated with carbon dioxide to convert any excess of alkali into the acid carbonate. We have found, however, that it is easier to titrate the hydrocyanic acid with iodine in presence of sodium hydrogen carbonate than to titrate the alkali cyanide under these conditions, and consequently we have modified the process by adding to the liquid to be titrated excess of sodium hydrogen carbonate. As this method of titration has rarely been used previously, we have confirmed the results so obtained by gravimetric estimations of the amount of hydrocyanic acid in the distillate.

| Colour of beans.  | Hydrocyanic acid produced,<br>estimated by the modified |                                 |
|-------------------|---------------------------------------------------------|---------------------------------|
|                   | Fordos and Gelis<br>method, per cent.                   | Estimated as<br>silver cyanide. |
| Dark brown.....   | { 0.0872                                                | —                               |
|                   | { 0.0955                                                | 0.1020                          |
| Purple .....      | { 0.088                                                 | —                               |
|                   | { 0.088                                                 | —                               |
| Light brown ..... | 0.041                                                   | 0.0503                          |

It thus appears that the beans with dark brown or purple markings furnish more prussic acid than the beans with light brown markings, and that the largest amount produced was equivalent to about one-tenth per cent. calculated on the dry beans.

*Isolation and Determination of the Constitution of the Glucoside  
Phaseolunatin.*

The finely powdered beans were exhausted by cold percolation with purified methylated alcohol. The mixed alcoholic liquors were then concentrated to a syrup, which was boiled repeatedly with water in order to separate the glucoside from resin. Tannin, gum and extractive matters were removed from the solution by precipitation with lead acetate, the excess of the latter being subsequently eliminated as lead

\* 'Journ. de Chimie et de Pharmacie,' vol. 23, p. 48.



sulphide. The colourless liquid so obtained was evaporated in a vacuum desiccator, the syrupy residue being well stirred every day, until it solidified to a mass of colourless acicular crystals, which were freed from the viscous mother liquor by absorption of the latter in a porous tile. The glucoside was purified by recrystallisation from water. It readily forms super-saturated solutions with this solvent, from which it separates only after vigorous stirring. The glucoside is almost insoluble in absolute alcohol, ether and petroleum, but is slightly soluble in acetone, chloroform and ethyl acetate; it also dissolves in alcohol containing water, but does not readily crystallise from such solutions even when concentrated. The glucoside crystallises in spreading rosettes of colourless needles from  $\frac{1}{2}$  to 1 inch in length, which melt at  $141^{\circ}$  C.

Combustions of specially purified material dried at  $100^{\circ}$  C. until of constant weight gave the following results:—

0.2277 gramme gave 0.4047 gramme  $\text{CO}_2$  = 48.3 per cent. C.

0.1412 „  $\text{H}_2\text{O}$  = 6.8 „ H.

0.1537 gramme gave 0.2710 „  $\text{CO}_2$  = 48.08 „ C.

0.0972 „  $\text{H}_2\text{O}$  = 7.02 „ H.

The formula  $\text{C}_{10}\text{H}_{17}\text{O}_6\text{N}$  requires C 48.1 per cent.; H 6.8 per cent.

The correctness of this formula has been confirmed by estimations of the dextrose produced on hydrolysis. To this glucoside we propose to assign the name—Phaseolunatin.

#### *Specific Rotation of Phaseolunatin.*

This constant was determined by observing the rotations produced by a 2.7608 per cent. solution in water contained in a 20 cm. tube. The mean of ten readings was:—

$$-1^{\circ} 27',$$

whence the specific rotation is

$$[\alpha]_D = -26^{\circ}.2.$$

#### *Action of Acetic Anhydride on Phaseolunatin.*

About 0.5 gramme of the glucoside was dissolved in 5 c.c. of acetic anhydride, the solution warmed on the water bath for 2 hours, then poured into alcohol and the mixture warmed until the oily precipitate first formed became hard and granular. After filtering, the precipitate was dissolved in water, the solution decolorised with animal charcoal and evaporated to a syrup in a vacuum desiccator. The sticky residue could not be crystallised; it was neutral in reaction, gave ethyl acetate on hydrolysis with concentrated sulphuric acid in presence of alcohol, and was probably, therefore, an acetyl derivative of the glucoside.

*Hydrolysis of Phaseolunatin by Acids.*

The hydrolysis was usually effected by heating the glucoside in aqueous solution with dilute hydrochloric acid at 100° C under a reflux condenser. The resulting solution had a strong odour of hydrocyanic acid and afforded a distillate giving the usual reactions of this substance. This distillate also gave a precipitate of iodoform on the addition of an alkali hydroxide followed by solution of iodine. The hydrocyanic acid was removed by conversion into Prussian blue, which was filtered off, the filtrate made slightly alkaline and distilled until the iodoform reaction was no longer obtained. To the distillate, hydroxylamine hydrochloride and a slight excess of sodium carbonate were added and the mixture after standing 2 hours shaken with ether. The ethereal liquid was separated, dried thoroughly over calcium chloride and allowed to spontaneously evaporate. A colourless crystalline substance then remained which melted at 58°, and had the characteristic odour of *acetoxime*. The latter is, however, not a satisfactory derivative for the identification of such small quantities of acetone as were present, and recourse was therefore had to the preparation of dibenzylidene acetone. To some of the purified distillate freed from hydrocyanic acid in the manner indicated were added a few drops of a 10-per-cent. aqueous solution of potassium hydroxide, followed by a similar quantity of benzaldehyde and sufficient ethyl alcohol (free from acetone) to produce a clear solution. This mixture on standing became cloudy, and in a few hours deposited a crop of golden yellow lamellæ which melted at 112° and exhibited all the properties of *dibenzylidene acetone* (m.p. 112°).

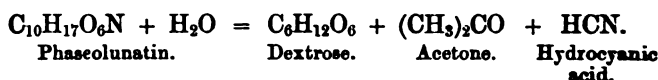
The remainder of the distillate was neutralised and evaporated to a small volume, decolorised with animal charcoal and examined in a polarimeter. The observed rotation was dextrorotatory, but the dark colour of the solution precluded a quantitative determination of its amount. When heated with a little phenylhydrazine at 100° C. this liquid afforded an osazone, which when recrystallised from alcohol melted at 206° (phenylglucosazone melts at 206°).

*Estimation of Sugar produced by Acid Hydrolysis.*

0.1746 gramme of the glucoside was dissolved in 100 c.c. of water. Portions of this solution were heated with dilute hydrochloric acid at 100° for varying periods. It was found that under these conditions about 2½ hours were required for complete hydrolysis.

| Quantity<br>of glucoside<br>used. | Time<br>of heating. | Dextrose found.               | Dextrose<br>produced, per<br>cent. |
|-----------------------------------|---------------------|-------------------------------|------------------------------------|
| 0.0524                            | 2 hours             | $0.0699 \times 0.5042$ gramme | 67.3                               |
| 0.0524                            | 2 "                 | $0.0714 \times 0.5042$ "      | 68.7                               |
| 0.0698                            | $2\frac{1}{2}$ "    | $0.0975 \times 0.5042$ "      | 70.4                               |
| 0.1309                            | 3 "                 | $0.1676 \times 0.5042$ "      | 64.6                               |

The equation



requires the production of 72.5 per cent. of dextrose.

#### *Alkaline Hydrolysis of Phaseolunatin. Phaseolunatinic Acid.*

When the glucoside is heated in aqueous solution with solutions of potassium, sodium or barium hydroxides, it undergoes hydrolysis, with the production of ammonia and the formation of a new acid glucoside, phaseolunatinic acid. This, like most compounds of the same class, *e.g.*, amygdalinic, lotusinic and dhurronic acids, is an amorphous gum-like substance, furnishing gum-like salts which are soluble in water, but insoluble in absolute alcohol. The sodium salt may be obtained pure by adding phaseolunatin to a solution of sodium ethoxide in alcohol. The glucoside at first dissolves, but almost immediately afterwards there is formed an amorphous white precipitate of the sodium salt. This retains a pulverulent form so long as it remains in the dry alcohol, but on removal from the liquid by filtration it begins to absorb water and becomes gum-like. The constitution of this acid glucoside was arrived at by an investigation of the products obtained from its hydrolysis by acids.

About 2 grammes of the original glucoside was heated at 100° C. for two hours with excess of baryta water. On evaporation there remained a varnish-like residue of the barium salt of the acid glucoside. To this excess of dilute sulphuric acid was added, the precipitated barium sulphate removed by filtration and the filtrate boiled for 15 minutes under a reflux condenser. The liquid was cooled, extracted with ether, the ethereal solution dried over calcium chloride and the solvent distilled off, when there remained an oil of an unpleasant rancid odour. This was boiled with water, the aqueous solution after filtration neutralised with baryta water and evaporated to a small volume, when minute colourless glistening plates of a barium salt separated. This on analysis gave the following result:—

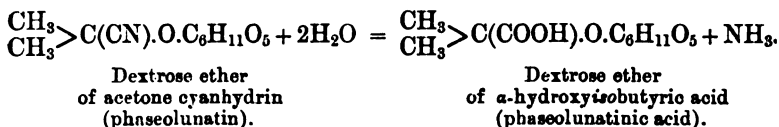
0.1569 gramme gave  $0.1077 \text{ BaSO}_4 = 68.73$  per cent.  $\text{BaSO}_4$ .

Barium  $\alpha$ -hydroxyisobutyrate,  $[(\text{CH}_3)_2\text{C}(\text{OH})\text{COO}]_2\text{Ba}$ , requires 68.01 per cent.  $\text{BaSO}_4$ .

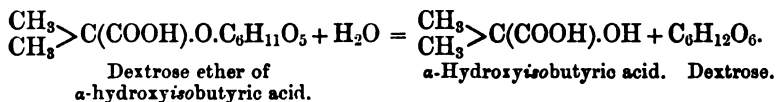
The residual liquid left after extraction with ether reduced Fehling's solution, and when warmed with phenylhydrazine gave a crystalline precipitate of phenylglucosazone, melting at 206°

Phaseolunatinic acid is thus proved to be the dextrose ether of  $\alpha$  hydroxyisobutyric acid.

The alkaline hydrolysis of phaseolunatin therefore takes place according to the following equation:—



The acid glucoside thus formed then undergoes hydrolysis by acids in the following manner:—



It is therefore proved that phaseolunatin is the dextrose ether of acetone cyanhydrin.

#### *The Enzyme of Phaseolus lunatus.*

The hydrolytic enzyme of *Phaseolus lunatus* was isolated in the usual manner by pouring an aqueous extract of the plant (containing chloroform as a preservative) into excess of alcohol and collecting the precipitated proteid matter. This precipitate was then re-dissolved in water and re-precipitated by alcohol. Prepared in this way the enzyme is an amorphous white powder almost completely soluble in water; it readily hydrolyses amygdalin, salicin, and phaseolunatin. The latter is also hydrolysed by the emulsin of sweet almonds, so that it is probable that the enzyme of *Phaseolus lunatus* is emulsin, although in the present state of our knowledge of the composition and reactions of enzymes it is impossible to prove with certainty the identity of two enzymes of different origin.

In the two previous papers of this series,\* it has been pointed out that the presence of cyanogenetic glucosides in *Lotus arabicus* and *Sorghum vulgare* is confined to those parts of the plant in which metabolism is actively proceeding, and that the glucoside no longer occurs when the plant attains maturity, and is not present in the seeds. In the case of *Sorghum vulgare*, cultivation does not appear to diminish the production of the glucoside. *Phaseolus lunatus* presents a different group of facts since, as M. Bonamé has shown, the mature semi-

\* 'Phil. Trans.,' B, vol. 194, 1901, p. 515, and A, vol. 190, 1902, p. 393.

cultivated plant furnishes prussic acid, and, as is proved in the present communication, the seeds of the wild Mauritius plant contain considerable quantities of the cyanogenetic glucoside phaseolunatin, which, however, is not found in the seeds of the same plant after systematic cultivation.

#### *Rangoon Beans.*

Whilst the investigation of the glucoside of *Phaseolus lunatus* was in progress, there were received at the Imperial Institute several specimens of beans imported into this country from Burma for the manufacture of a feeding stuff for cattle under the names of "Rangoon," "Burma," or "Paigya" beans. These beans varied in colour from light to dark brown with purple patches, and closely resembled the seeds of *Phaseolus lunatus* both in appearance and size, and are, no doubt, derived from this plant. On examination in the manner previously described, Rangoon beans yielded small quantities of hydrocyanic acid, amounting usually to not more than 0.004 per cent. The isolation of the small quantity of glucoside represented by such a proportion of hydrocyanic acid was not possible, but evidence of the existence of the glucoside phaseolunatin was obtained by extracting several pounds of the beans and hydrolysing the extract with dilute hydrochloric acid, when a distillate containing both hydrocyanic acid and acetone was obtained, the latter being identified by its conversion into dibenzylidene acetone.

#### *General Considerations.*

The present investigation had for its principal object the determination of the question as to whether the production of prussic acid in the seeds of *Phaseolus lunatus* originated with a glucoside, and if so to isolate this constituent and ascertain its chemical composition. Phaseolunatin proves to be a cyanogenetic glucoside with an aliphatic nucleus, and in this respect differs from the glucosides of this class already known, viz., amygdalin, lotusin and dhurrin, which contain aromatic (benzenoid) nuclei.

The occurrence in *Phaseolus lunatus*, apparently throughout its life history, of a cyanogenetic glucoside, together with the enzyme appropriate for its hydrolysis, seems to strengthen the view expressed by us in a previous paper, that these glucosides must play some definite part in the metabolism of plants.

Treub, as the result of his investigations of the production and distribution of hydrocyanic acid in *Pangium edule*, suggested that the immediate precursor (probably a cyanogenetic glucoside) of the acid in this plant is a formative material utilised in the synthesis of proteid. In this connection it is of interest to note the ease with which cyanogen

compounds of this type can, by processes of reduction, be converted into amino-derivatives, which recent researches indicate as the materials from which, by processes of condensation, proteids originate.

his supposition implies that cyanogenetic glucosides are to be regarded as plastic materials, whilst the enzymes with which they are associated must be considered as aplastic substances with the definite function of decomposing and possibly also producing cyanogenetic glucosides, since the hydrolytic action of enzymes appears to be reversible.

This suggestion may explain the occurrence of cyanogenetic glucosides in *Lotus arabicus* and *Sorghum vulgare* during that period of their life-history in which metabolism is active and their disappearance when the plants have matured and produced seeds, since this period coincides with that in which the synthesis of proteid in the plant is actively proceeding. Although *Phaseolus lunatus* resembles *Lotus arabicus* and *Sorghum vulgare* in containing a cyanogenetic glucoside, it differs from these plants in continuously secreting this glucoside which is likewise found in the seeds. In this respect *Phaseolus* resembles the bitter almond. The seed produced by *Phaseolus lunatus* under cultivation, however, does not contain phaseolunatin, just as the seed of the sweet almond, which there is reason to believe is produced by the cultivation of *Prunus amygdalus*, contains no amygdalin. It is impossible without further knowledge of the causes which influence plants in the selection of reserve materials to offer any explanation of the fact that these glucosides appear as reserve materials in the seeds of *Phaseolus lunatus* and in those of the bitter almond, but not in those of *Lotus arabicus* and *Sorghum vulgare*.

The reason for the disappearance of cyanogenetic glucosides from the seeds of *Phaseolus lunatus* and the bitter almond when cultivated, is probably to be found in the stimulus to metabolism resulting from improved nutrition and environment. These, as is well known, lead to the more rapid utilisation of plastic substances, with the result that there is very little, or possibly none, of the cyanogenetic glucoside available for storage as reserve material in the seeds of the cultivated plant. The enzymes on the other hand are aplastic substances performing definite synthetical and analytical functions without themselves undergoing change, and consequently it is to be expected that they would be found alike in the seeds of the wild and of the cultivated plants. The enzyme emulsin occurs in the seeds of the cultivated *Phaseolus lunatus* as well as in those of the sweet almond, although the cyanogenetic glucoside has disappeared under the influence of cultivation.

The observations recorded by the authors in a previous paper,\* with regard to the existence of the cyanogenetic glucoside dhurrin in

\* Part II, loc. cit.

*Sorghum vulgare* and the consequent production of prussic acid by this plant, have led to the examination by J. C. Brunnich,\* Chemist to the Agricultural Department, Brisbane, of the varieties of this plant grown in Queensland, which have been long known to be poisonous to cattle under certain conditions, although the nature and origin of the poison had not been discovered. Brunnich has now determined the amounts of hydrocyanic acid produced when weighed quantities of the plants grown under different conditions are crushed with water. The results thus obtained confirm those already recorded by the authors in the case of sorghum grown in Egypt, and show that the amount of cyanogenetic glucoside contained in the stem and leaves of the plant increases until the seeds are ripe, after which it rapidly diminishes until the glucoside finally disappears. Brunnich finds that cultivation of sorghum on land heavily manured with sodium nitrate leads to an increased production of the cyanogenetic glucoside in the stem and leaves.

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“The Differential Invariants of Space.” By Professor A. R. FORSYTH, Sc.D., LL.D., F.R.S. Received June 18,—Read June 18, 1903.

(Abstract.)

The memoir is devoted to the consideration of the differential invariants of ordinary space and of a surface or surfaces in that space; they are the functions of the fundamental magnitudes of space and of quantities connected with the surface or surfaces which remain unaltered in value through all changes of the independent variables of position.

The method used arises through the obviously natural development of the method used for the corresponding investigations concerned with a surface and with curves upon the surface, which formed the subject of an earlier memoir by the author. The partial differential equations, characteristic of the invariance, are formed, and then the most general solution of these equations is constructed. At a certain stage in the latter process, the equations then remaining unsolved can be transformed, so that they become the invariants and the contravariants of a set of simultaneous ternary forms. The results of the latter theory are then used to complete the solution of the equations.

The main part of the memoir is devoted to obtaining the invariants; and the explicit expressions of the invariants, up to the third order inclusive as associated with a single surface, are given. Further,

\* ‘Trans. Chem. Soc.’, 1903.

those which are associated with two surfaces are obtained up to the second order inclusive. The necessary calculations are laborious. In the case of the invariants, which are actually of the third order, only the results are stated; they were obtained by solving fifty-seven simultaneous partial differential equations.

It is known from Lamé's investigations that there are six equations characteristic of the fundamental magnitudes when the independent variables are the parameters of a triply-orthogonal system of surfaces. Cayley proved that there are similarly six equations when the independent variables are the parameters of three families of surfaces not orthogonal to one another. These six equations, as formed by Cayley, arise in the course of the construction of the invariants of the third order.

In the later part of the memoir, the invariants up to the second order inclusive are geometrically interpreted. Those of the third order have not yet been similarly interpreted; geometrical considerations are added to show that, when the significance of these invariants is established, two new fundamental equations among the quantities connected with a surface will be found to exist.

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"The Ultra-violet Spectrum of Radium." By Sir WILLIAM CROOKES, F.R.S. Received August 1, 1903.

[PLATES 16—18.]

The spectrum of radium has been examined and the wave-lengths of many of its lines given by several observers, amongst whom I may include Exner and Haschek,\* Berndt,† Demarçay,‡ and Runge.§

Between these observers, however, there are great discrepancies, lines given by one being absent in other lists, and the wave-lengths even of strong lines varying between wide limits. Being in possession of perhaps the purest radium hitherto employed for spectrum work, I have used some of it in photographing its ultra-violet spectrum. The negatives so obtained have enabled me to get measurements from which the wave-lengths of the lines have been calculated with an accuracy only limited by the accuracy of the iron lines used as standards.

\* Franz Exner and E. Haschek, 'Wien Akad. Sitzber.,' vol. 110, July, 1901; 'Chem. News,' vol. 86, p. 247.

† G. Berndt, 'Physikalische Zeitschrift,' 2 Jahrg., No. 12; 'Chem. News,' vol. 83, p. 77.

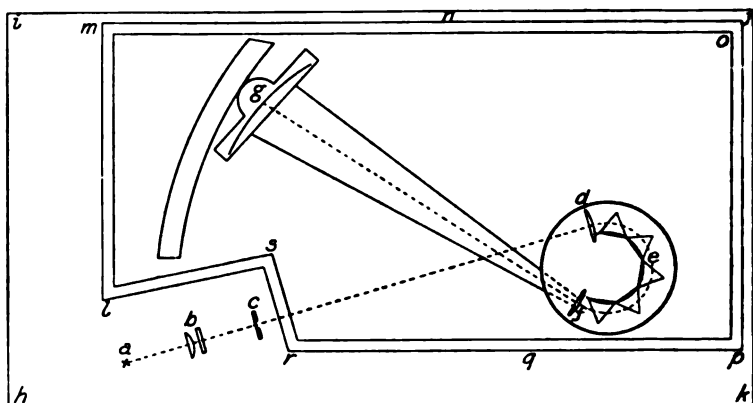
‡ Demarçay, 'Comptes Rendus,' vol. 129, p. 716; vol. 131, p. 258.

§ C. Runge, 'Astrophysical Journal,' vol. 12, p. 1.



The spectrograph itself is a five-prism quartz instrument which I have had in use since 1894. A general idea can be gained of the arrangement of the spectrograph from the accompanying outline plan (fig. 1). The light from the source, *a*, passes first through the condenser, *b*, on to a slit, *c*, thence to the collimating lens, *d*, and

FIG. 1.



round the train of prisms, *e*. It then passes through the camera lens, *f*, whence it falls on the sensitive film in the holder, *g*. The whole apparatus is mounted on a planed cast-iron table, *h, i, j, k*, 49½ inches long, 31 inches wide, and 1½ inches thick. The prisms, lenses, and photographic film-holder are enclosed in a large wooden framework, *l, m, n, o, p, q, r, s*, having aluminium shutters on each side, so that the inner adjustments can be effected easily. The height of the enclosure is 28 inches, and the whole is perfectly light-tight when the shutters are down. Outside the dark enclosure, in the space *h, l, s, r*, are situated the arrangements for producing the light to be examined, the optical condensers, and the slit.

An electrical condenser of 180 square inches is intercalated in the secondary circuit, and a coil of twelve turns of well-insulated wire, each turn being 12 inches in diameter, is interposed in the path of the secondary current. This introduction of self-induction in the circuit suppresses most of the air lines, and gives the metal lines on a black background.

The optical efficiency of a spectrograph depends in no small degree on the way in which the source of light is presented to the slit. If the electrodes are too far apart there is distortion, owing to each pole forming its own luminous centre, and if the spark is close to the slit we have to contend with other irregularities; the image is not clear, and the lines are often confused and blurred. If the spark is

moved away from the slit the spectrum gains in definition; the greater the distance between the light and the slit the finer is the sharpness and definition of the lines, but at the same time the loss of light is great. This loss of light, however, may be obviated in great measure, with considerable improvement of the definition, by inserting optical condensers between the spark and the slit. I use two condensers of quartz, plano-cylindrical, one being double the focus of the other, the axes intersecting each other at an angle of  $90^\circ$ ; the object being to concentrate a line instead of a point of light on the slit. All optical condensers waste much light. I use them more to obtain well-defined images than to abridge the time of exposure.

The slit is made of two shallow-angled quartz prisms, as I have already described,\* and the distance apart of the jaws is generally 0.01 mm.

The quartz prisms, of which there are five, are of  $60^\circ$ , made in two halves of  $30^\circ$  each, according to Cornu's plan, one half being right-handed and the other half left-handed. The contact surface of both bisects the refractive angle of the entire prism, and is placed perpendicularly to the crystalline axis of both prisms. In this way duplication of lines is avoided.

The sensitive film-holder must be set at an angle varying with the portion of the spectrum being photographed, as the focus of the less refrangible is longer than that of the more refrangible rays. Moreover, the focal plane is not flat, so the film itself must follow the diacaustic curve, or the lines on it will not all be in focus together.† For this reason glass plates cannot be used, and celluloid films are employed.

To obtain the best definition of any desired line for measurement, expose for a long time and develop briefly, using plenty of potassium bromide in the pyro developer. It is impossible to photograph properly the whole spectrum with a single exposure, so as to have it well defined in all parts, since the brightest lines are over exposed and blurred sideways before the faint ones are impressed. This important fact is too generally lost sight of in spectrum photography.

For correct determination of wave-lengths, it is necessary to photograph on the same film the spectrum of a metal whose lines are known. I generally use iron for this purpose; it has the advantage of giving a large number of very fine lines, the wave-lengths of which have been accurately measured, and not being very volatile, the poles do not rapidly wear away. By means of diaphragms close to the slit the experimental and the standard spectra are photographed on the same

\* 'Chemical News,' vol. 71, p. 175, April 11, 1895; 'Roy. Soc. Proc.,' vol. 65, p. 241.

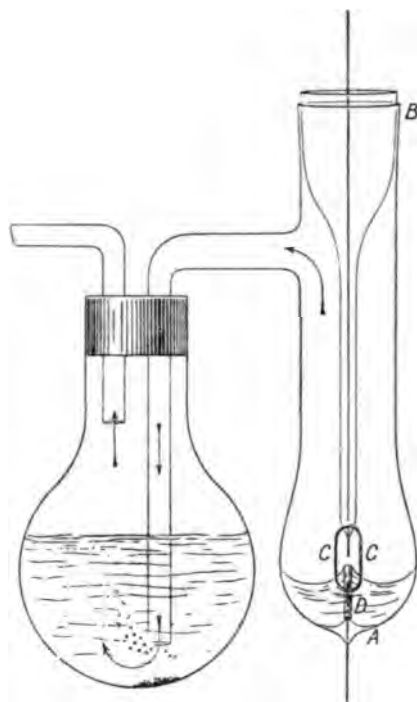
† 'Chem. News,' vol. 72, p. 87, August, 1895; and vol. 74, p. 259, November, 1896; 'Proc. Roy. Soc.,' vol. 65, p. 242.

film, overlapping for about 1 mm. in the centre.\* The photographs are then transferred to a measuring machine, and from the figures thus obtained the wave-lengths are calculated.

The radium was used in the form of nitrate, a well-crystallised salt easily soluble in water. The induction spark was taken between platinum poles partly immersed in a strong solution of the salt. On this account the nitrate was used in preference to the chloride. Much platinum is always dissolved when the poles are sparked in a solution of a chloride, while with nitrates this does not occur to the same extent.

The solution was strong, and slightly acid with nitric acid. Many forms of spark tube were tried before a satisfactory form (shown in fig. 2) was devised. AB is a tube of hard Jena glass, with a bulb at

Fig. 2.



the lower end. At the bottom of the bulb a platinum wire is sealed in, and in the upper part of the tube, at B, a short piece of tube is ground in to form a stopper. A long platinum wire passes through from this stopper, bare at the upper part, and guarded with glass

\* 'Roy. Soc. Proc.,' vol. 65, p. 243.

inside the bulb tube. A hole, CC, is made at one side of the bulb to form a window, and a piece of platinum tube is put round the lower platinum wire at D, so that its upper end is about 3 mm. above the end of the wire it surrounds, and a millimetre below the centre of the window, CC. The upper wire should be about 1 mm. from the top of the platinum tube surrounding the lower wire. Any solution put in the lower part of the bulb is sucked up by capillarity to the top of the platinum tube, and an induction spark between the two wires gives a spectrum of any metal in solution. When exposures of more than ten minutes or so are required, it is necessary to introduce fresh solution to keep the level in the bulb constant. This is easily done during the exposure by means of a small pipette. The splash of the spark throws drops of liquid for some distance, and the heat and decomposition cause nitric acid to come off. These are objectionable when falling on delicate apparatus, and they cause great waste of solution, which with rare bodies is to be avoided; to prevent this a branch tube is sealed in near the top of the spark tube, dipping to the bottom of a flask through a cork. Another tube passes just through the cork and is connected with an aspirator. During the sparking operation a rapid current of air is drawn in through the window, and all splashes and vapours are washed through the water in the wash-bottle. Thus the acid fumes are kept from injuring the apparatus, and the valuable salt is saved in the wash water.

The presence of platinum lines is due to the platinum poles between which the spark is taken. They are easily identified by photographing a platinum spectrum and a platinum-radium spectrum on the same plate, slightly overlapping one another. The platinum being common to both, gives continuous lines across the two spectra, while the radium lines only appear in one spectrum. Radium being purified from barium by a tedious process of fractional crystallisation of the bromides is almost certain to show barium lines in its spectrum. I have only been able to use about a grain of perfectly pure radium bromide, all other samples containing traces of barium.

Owing to the length of the spectrum and the necessity of having the lines near the position of minimum deviation to get the greatest sharpness, each photograph is limited to a small extent of spectrum, and eight exposures are needed to take in the whole ultra-violet spectrum, and as far into the visible part as the plates are sensitive to.

The following table gives the wave-lengths of all the lines ascribed to radium by different observers. Many of the early observations are necessarily imperfect, owing to the enormous difficulty of preparing radium compounds of sufficient strength to show a photographed spectrum. And when sufficient concentration was obtainable, the observations were necessarily limited, owing to the minute amount available rendering verification difficult.

Wave-lengths of the Radium Lines according to the different Authorities.

| Runge.   | De-<br>marçay. | Exner<br>and<br>Haschek. | W.<br>Crookes. | Inten-<br>sity. | Remarks.                                                                                                                                                                                    |
|----------|----------------|--------------------------|----------------|-----------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|          |                | 2512·46                  |                |                 | I cannot see this line on my photo-<br>graphs.                                                                                                                                              |
|          |                |                          | 2709·06        | 20              | This is close to an iron line,<br>2709·14.                                                                                                                                                  |
|          |                | 2736·2                   |                |                 | I cannot see this line on my photo-<br>graphs.                                                                                                                                              |
|          |                | 2813·60                  | 2813·876       | 30              | Comes between a fine pair of<br>platinum lines.                                                                                                                                             |
|          |                | 2816·25                  |                |                 | Probably a platinum line, 2816·1.                                                                                                                                                           |
|          |                | 2831·98                  |                |                 | I cannot see this line on my photo-<br>graphs.                                                                                                                                              |
|          |                | 2877·10                  |                |                 | Probably an iridium line, 2877·1.                                                                                                                                                           |
|          |                | 2908·0                   |                |                 | Probably a platinum line, 2908·1.                                                                                                                                                           |
|          |                | 2976·17                  |                |                 | Probably a platinum line, 2976·9.                                                                                                                                                           |
|          |                | 3079·97                  |                |                 | Probably a platinum line, 3079·8.                                                                                                                                                           |
|          |                | 3126·63                  |                |                 | I cannot see this line on my photo-<br>graphs.                                                                                                                                              |
|          |                | 3541·77                  |                |                 | Ditto.                                                                                                                                                                                      |
| 3649·77  | 3649·6         | 3649·33                  | 3649·712       | 70              | A very strong radium line.                                                                                                                                                                  |
|          |                |                          | 3809·393       | 10              | A faint radium line.                                                                                                                                                                        |
|          |                |                          | 3812·170       | 5               | A faint radium line.                                                                                                                                                                        |
| 3814·591 | 3814·7         | 3814·62                  | 3814·661       | 100             | The strongest line in the radium<br>spectrum.                                                                                                                                               |
|          |                | 3861·77                  |                |                 | I cannot see this line on my photo-<br>graphs. Exner and Haschek<br>include it in their radium lines,<br>but in a note say it is not a line<br>of radium.                                   |
|          |                |                          | 3961·627       | 5               | A faint radium line.                                                                                                                                                                        |
|          |                | 3993·25                  |                |                 | Probably a barium line, 3993·69.                                                                                                                                                            |
|          |                |                          | 4010·397       | 10              | A faint radium line.                                                                                                                                                                        |
|          |                | 4053·81                  | 4053·124       | 10              | A faint radium line.                                                                                                                                                                        |
| 4341·0   | 4340·6         |                          | 4340·619       | 5               | A faint radium line.                                                                                                                                                                        |
|          | 4364·2         |                          |                |                 | I cannot see this line on my photo-<br>graphs.                                                                                                                                              |
| 4436·45  | 4436·1         |                          |                |                 | Probably a platinum line, 4437·5.                                                                                                                                                           |
|          | 4458·0         |                          |                |                 | Demarçay says this is the centre<br>of a nebulous band, which be-<br>gins at 4463·7, has a maximum<br>from 4458·4 to 4455·2, and ends<br>at 4390·0. I cannot see this<br>on my photographs. |
| 4533·33  | 4533·5         |                          |                |                 | I cannot see this line on my photo-<br>graphs.                                                                                                                                              |
|          | 4600·3         |                          |                |                 | Demarçay says (with a query) that<br>this line does not belong to<br>radium. I cannot see it on my<br>photographs.                                                                          |
|          | 4627·4         |                          |                |                 | Demarçay says this is the centre<br>of a nebulous line, which be-<br>gins sharply at 4621·9, has a<br>maximum at 4627·5, and ends<br>about 4631. I cannot see it<br>on my photographs.      |
|          | 4641·9         |                          |                |                 | I cannot see this line on my photo-<br>graphs.                                                                                                                                              |

Wave-lengths of the Radium Lines—*continued*.

| Runge.            | De-<br>marçay.                       | Exner<br>and<br>Haschek.  | W.<br>Crookes.     | Inten-<br>sity. | Remarks.                                                                                              |
|-------------------|--------------------------------------|---------------------------|--------------------|-----------------|-------------------------------------------------------------------------------------------------------|
| 4682·346          | 4683·0<br>4692·1<br>4699·8<br>4726·9 | 4682·41<br><br><br>4781·4 | 4682·149           | 25              | A strong radium line.<br>I cannot see this line on my photo-<br>graphs.<br>Ditto.<br>Ditto.<br>Ditto. |
| 4826·14<br>5813·9 | 4826·3                               |                           | 4825·896<br>5813·9 | 15              | A strong radium line.<br>This is a strong citron line, out-<br>side the range of my photo-<br>graphs. |

Measurements are taken of the exact distances apart of the radium lines and certain adjacent iron lines used as standards. By using a formula, first communicated to the British Association by Sir George Stokes, the wave-lengths of the unknown lines can be calculated. At the time the formula was given it was sufficiently accurate for the instrumental means employed for photographing spectra, but the formula only gave approximate results, and the accuracy of determination of wave-lengths has since improved so much that a correction is required to the original formula. Sir George Stokes, before whom I placed the difficulty in June, 1895, quickly solved it in a satisfactory manner. The usual formula requires the positions of two standard lines of known wave-length,  $n_1$  and  $n_3$ , on each side of the unknown line,  $n_2$ . To make the small correction, Sir George advised me to take a third line of known wave-length, chosen well removed from the selected known lines  $n_1$  and  $n_3$ . If chosen in the interval 1—3 it had better not be greatly distant from the middle. There is, however, very wide latitude of choice in this respect. All these lines must be photographed and measured in the usual way. Calculate the approximate wave-length of the unknown line by the original formula, and then calculate the approximate wave-length of the third known line by the same formula, *as if it were unknown*, using the two original standards for this purpose also. We have now the approximate wave-length of a known line, as given by the formula, and also its true wave-length. The difference between these two values leads (*infra*, p. 303) to the correction to apply to the approximate value of the unknown line.

It often happens that four or more lines are well placed for use as standards. If any three of these be taken, and from them the positions of the other lines be calculated, it will sometimes be found that there is a small residual error in some of them. In such a case the error can be minimised by adjusting the value of the three primary standards so

*Rule.*

First calculate the approximate value of  $\lambda_2$  by the following formula:—

$$\frac{\lambda_3^2 \lambda_1^2 (n_3 - n_1)}{\lambda_1^2 (n_2 - n_1) + \lambda_3^2 (n_3 - n_2)} = \lambda_2^2 \text{ (approx.)} \dots\dots (1).$$

Next, in a similar way, find the approximate value of  $\lambda_4$ , using the following formulæ:—

$$\frac{\lambda_3^2 \lambda_1^2 (n_3 - n_1)}{\lambda_1^2 (n_4 - n_1) + \lambda_3^2 (n_3 - n_4)} = \lambda_4^2 \text{ (approx.)} \dots\dots (2).$$

Then

$$\lambda_4 \text{ (true)} = \lambda_4 \text{ (approx.)} \pm E_4.$$

Now calculate  $E_2$  by the following equation:—

$$\frac{(\text{Approx.}) \lambda_3^3 (n_2 - n_1) (n_3 - n_2)}{(\text{Approx.}) \lambda_4^3 (n_4 - n_1) (n_3 - n_4)} E_4 = E_2 \dots\dots (3).$$

Then

$$(\text{Approx.}) \lambda_2 \pm E_2 = \lambda_2.$$

[In fact, writing  $y$  for  $\lambda^{-2}$ , of which the refractive index is a function, and  $x$  for  $n$ , the graph of the relation between  $y$  and  $x$  may in this neighbourhood be identified with a parabola. The formulæ (1) and (2) neglect the effect of its curvature, by taking the points 2 and 4 to be on the chord connecting the points 1 and 3. The corrections  $E_2$  and  $E_4$  are thus connected with the distances from the points on this chord to the true points on the curve by the formula  $\delta y = -2E/\lambda^3$ ; and the formula (3) connecting them is the expression of a well-known geometrical property of a parabola.]

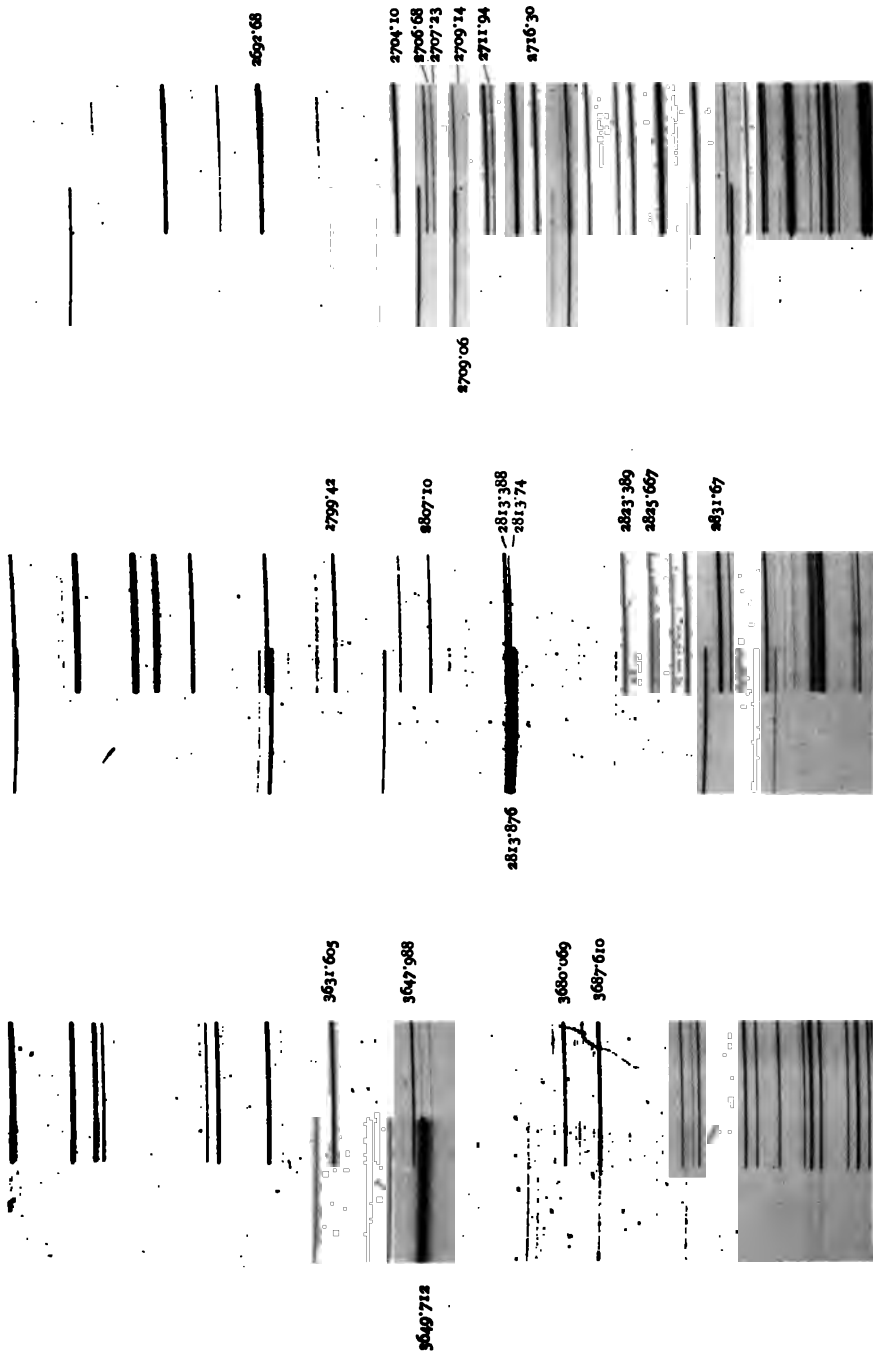
*Example.*

Calculate a radium line from adjacent iron lines as standards.

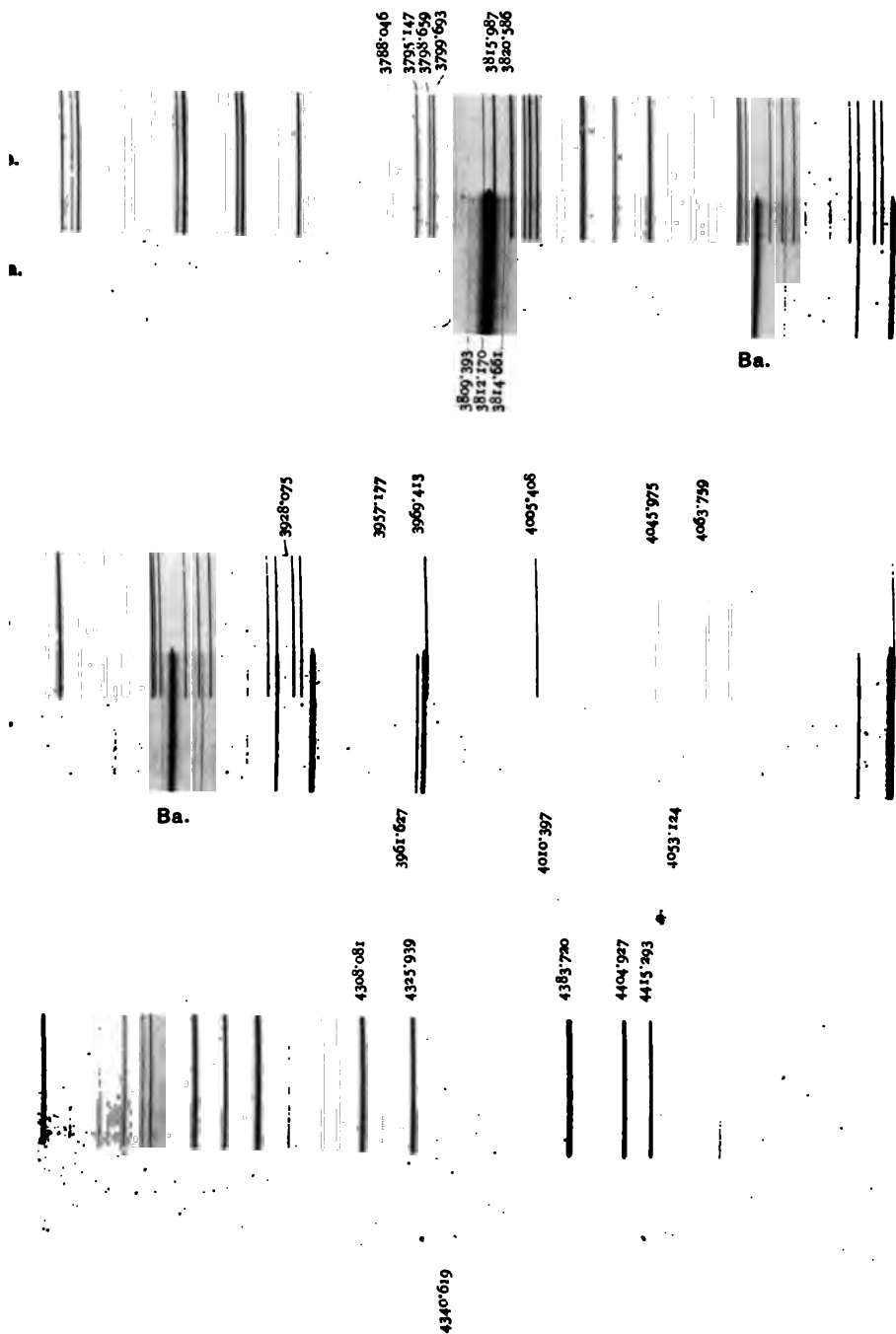
|                    |                                     |
|--------------------|-------------------------------------|
| $n_1 = 0.000000.$  | $\lambda_1 = 2813.388$ (Rowland).   |
| $n_2 = 0.005310.$  | $\lambda_2 = \text{A radium line.}$ |
| $n_4 = 0.107143.$  | $\lambda_4 = 2823.389$ (Rowland).   |
| $n_3 = 0.131020.$  | $\lambda_3 = 2825.667$ (Rowland).   |
| $2 \log \lambda_1$ | $2 \log \lambda_3$                  |
| $\log 0.00531$     | $\log 0.125710$                     |
| $\log 42029.46$    | $\log 1003718.32$                   |
| $4.6235538$        | $42029.46$                          |
|                    | $\log 1045747.78 = 6.0194283$       |

|                                                   |                                         |                               |           |
|---------------------------------------------------|-----------------------------------------|-------------------------------|-----------|
| $2 \log \lambda_3$                                | 6.9022420                               |                               |           |
| $2 \log \lambda_1$                                | 6.8984593                               |                               |           |
| $\log 0.131020$                                   | 1.1173376                               |                               |           |
| <hr/>                                             |                                         |                               |           |
| log numerator                                     | 12.9180389                              |                               |           |
| log denominator                                   | 6.0194269                               |                               |           |
| <hr/>                                             |                                         |                               |           |
| 2)                                                | 6.8986120                               |                               |           |
| <hr/>                                             |                                         |                               |           |
| $3.4493060 = \log 2813.883 = \lambda_2$ (approx.) |                                         |                               |           |
| <hr/>                                             |                                         |                               |           |
| $2 \log \lambda_1$                                | 6.8984593                               | $2 \log \lambda_3$            | 6.9022420 |
| $\log 0.107143$                                   | 1.0299638                               | $\log 0.023877$               | 2.3779798 |
| <hr/>                                             |                                         | <hr/>                         |           |
| $\log 848053.20$                                  | 5.9284231                               | $\log 190643.44$              | 5.2802218 |
|                                                   |                                         | 848053.20                     |           |
|                                                   |                                         | <hr/>                         |           |
|                                                   |                                         | $\log 1038696.64 = 6.0164887$ |           |
| log numerator                                     | 12.9180389                              |                               |           |
| log denominator                                   | 6.0164887                               |                               |           |
| <hr/>                                             |                                         |                               |           |
| 2)                                                | 6.9015502                               |                               |           |
| <hr/>                                             |                                         |                               |           |
| 3.4507751                                         | $\log 2823.418 =$ (approx.) $\lambda_4$ |                               |           |
| But—                                              | $\lambda_4 = 2823.389$                  |                               |           |
| $\therefore$                                      | $E_4 = 0.029$                           |                               |           |
| <hr/>                                             |                                         |                               |           |
| $3 \log \lambda_2$                                | 10.3479                                 | $3 \log \lambda_4$            | 10.3523   |
| $\log 0.005310$                                   | 3.7251                                  | $\log 107143$                 | 1.0300    |
| $\log 0.12571$                                    | 1.0994                                  | $\log 0.023877$               | 2.3780    |
| <hr/>                                             |                                         | <hr/>                         |           |
| log numerator                                     | 7.1724                                  |                               | 7.7603    |
| log denominator                                   | 9.2979                                  | $\log 0.029$                  | 2.4624    |
| <hr/>                                             |                                         | <hr/>                         |           |
|                                                   | 3.8745                                  |                               | 9.2979    |
|                                                   | $\therefore E_2 =$                      | 0.007                         |           |
|                                                   | $\lambda_2 =$                           | 2813.876                      |           |

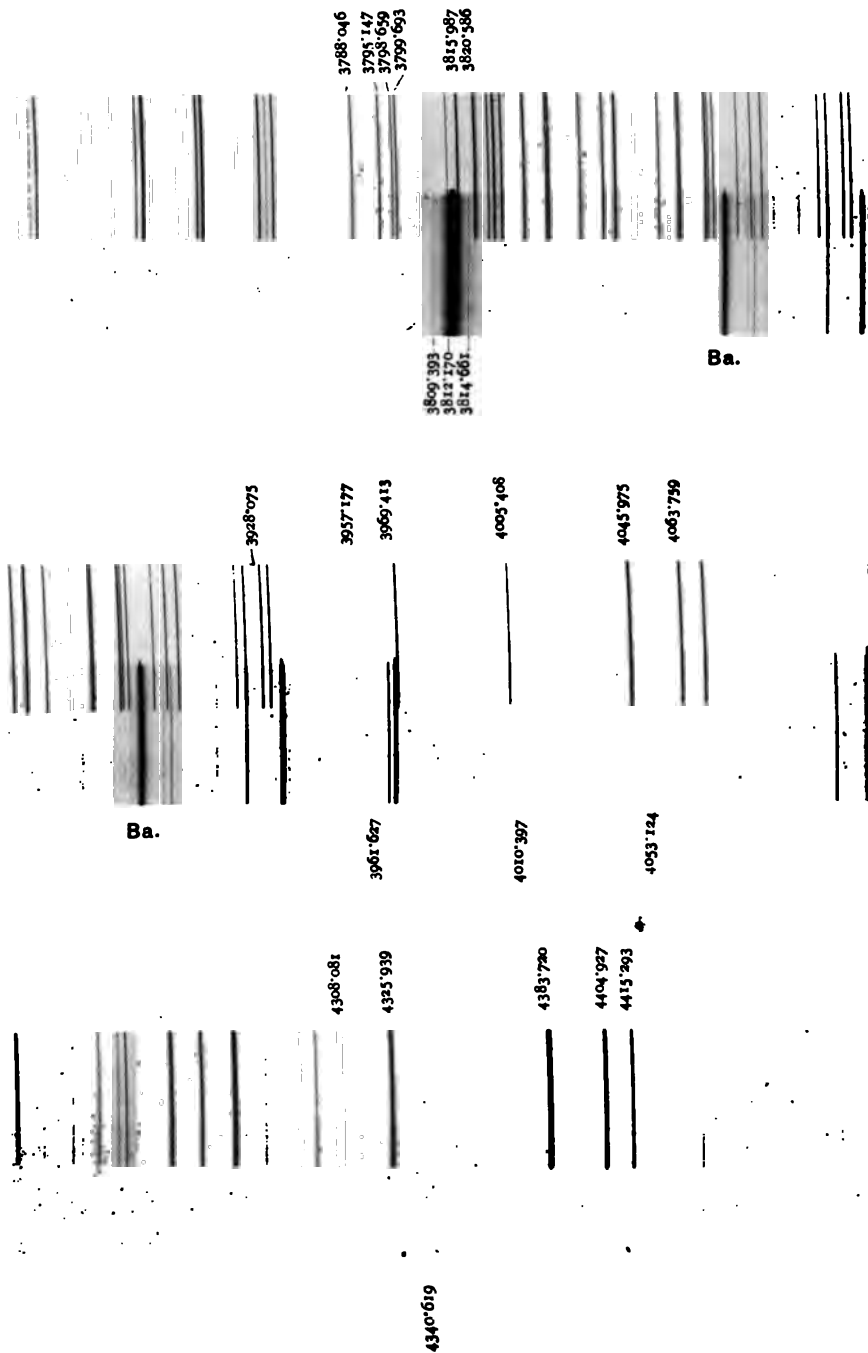














"On the Physiological Action of the Poison of the Hydrophidæ. Part II.—Action on the Circulatory, Respiratory, and Nervous Systems." By LEONARD ROGERS, M.D., B.S. (Lond.), M.R.C.P., F.R.C.S., I.M.S., late acting Professor of Pathology, Medical College, Calcutta. Communicated by Dr. A. D. WALLER. F.R.S. Received June 6,—Read June 18, 1903.

(From the Physiological Laboratory of the University of London.)

In my previous paper I dealt with the action of the poison of the Sea snakes as far as it was possible to examine it under the conditions of work in Calcutta, and reserved the consideration of certain questions until I was able to test them with the aid of a well-equipped laboratory. This I have now been able to do in the Physiological Laboratory of the London University, by the courtesy of Dr. A. D. Waller, with results which appear to be worthy of being placed on record in a further paper.

*Blood Pressure and Respiratory Curves.*

The effects of the poison on the blood pressure and on the rate and amplitude of the respirations have been studied by taking tracings of the former by a Gad's manometer and of the latter with Sandström's recorder, large but varying doses being administered intravenously in chloroformed cats and rabbits. The results uniformly showed a primary failure of respiration followed by a marked rise of blood pressure with the increasing venosity of the blood, respiratory convulsions (except when the respiratory failure was extremely rapid), and a final sudden fall of blood pressure some minutes after complete cessation of respiration. The general results obtained may be conveniently summarised in the following table :—

| No.   | Animal.  | Dose per kilo. | Respiration failing. | Blood pressure rising. | Respiration ceased. | Convulsions ceased. | Blood pressure fell rapidly. |
|-------|----------|----------------|----------------------|------------------------|---------------------|---------------------|------------------------------|
|       |          | mgram.         | min.                 | min.                   | min.                | min.                | min.                         |
| 1.... | Cat..... | 1              | 6                    | 8                      | 12                  | 8                   | 12½                          |
| 2.... | Rabbit.. | 1              | 3½                   | 6                      | 9                   | 10½                 | 13½                          |
| 3.... | Rabbit.. | 2              | 2½                   | 4                      | 6                   | 6                   | 10                           |
| 4.... | Cat..... | 2              | 3                    | 4½                     | (?)                 | (10)                | (22)*                        |
| 5.... | Rabbit.. | 4              | 1                    | 1½                     | 2½                  | Nil                 | 3½                           |

\* Artificial respiration.

In the fourth experiment the onset of convulsions and the final failure of the circulation, as evidenced by the sudden fall in blood pressure, were both delayed by the use of artificial respiration. With this exception, it will be seen from the table that both the respiration and the circulation fail more and more rapidly as the dose of the poison is increased, until with a dose of 4 milligrammes per kilo. weight ( $1/250,000$  of the body weight) the respiration was affected in 1 minute and had entirely ceased in  $2\frac{1}{2}$  minutes, while the circulation failed in  $3\frac{1}{2}$  minutes. The exact sequence of events can be best illustrated by the data and tracings of the following two typical experiments, being Nos. 3 and 5 in the above table.

*Experiment 3.*

Rabbit, weight  $1\frac{1}{2}$  kilos., under chloroform. Cannula in the carotid artery, connected with a Gad's manometer. Respirations recorded with Sandström's instrument. 3 milligrammes (2 milligrammes per kilo. weight) of dried Enhydrina poison injected into the external jugular vein dissolved in 0.75 c.c. of 0.9 per cent. NaCl.

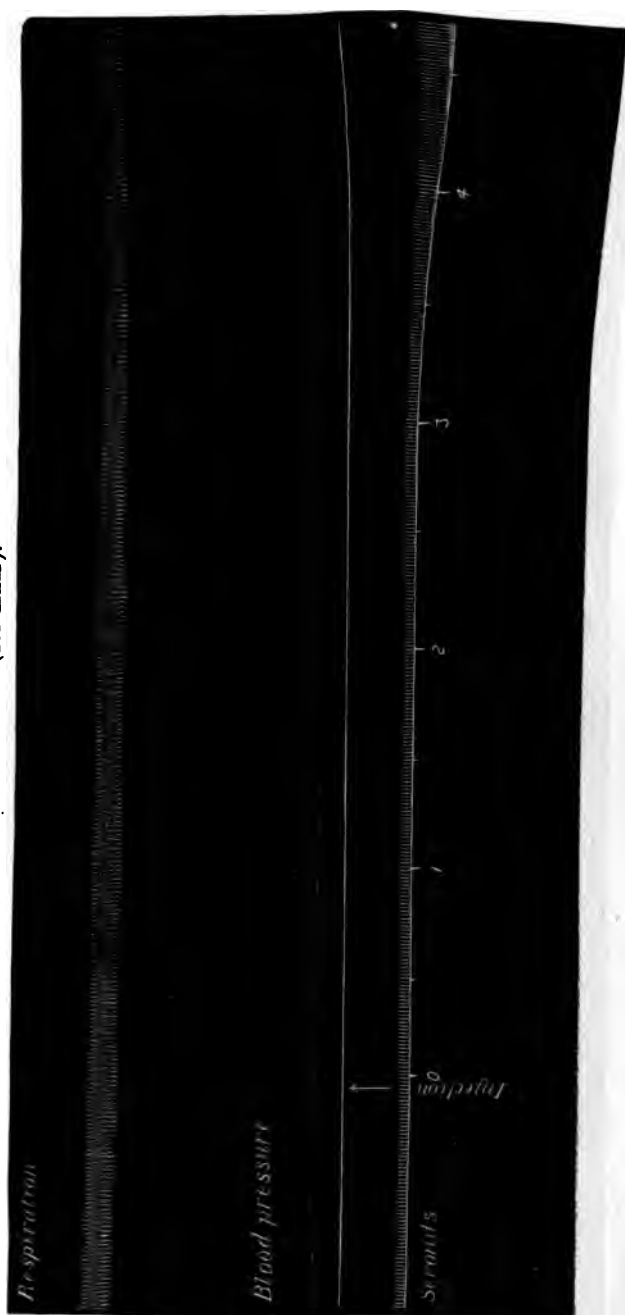
| Time.               | Blood pressure in mm. Hg. | Respirations per minute. | Amplitude of respirations. | Remarks.                |
|---------------------|---------------------------|--------------------------|----------------------------|-------------------------|
| Before injection .. | 92                        | 51                       | mm. 4                      |                         |
| After 1 min. ....   | 89                        | 50                       | 4                          |                         |
| " 2 " ....          | 91                        | 49                       | $3\frac{1}{2}$             |                         |
| " 3 " ....          | 94                        | 46                       | 3                          | Respiration failing.    |
| " 4 " ....          | 140                       | 43                       | $2\frac{1}{2}$             | Blood pressure rising.  |
| " 5 " ....          | 166                       | 39                       | 2                          |                         |
| " 6 " ....          | 180                       | 34                       | 1                          | Convulsions beginning.  |
| " 7 " ....          | 200                       | 21                       | $\frac{1}{2}$              | Respiration ceased.     |
| " 8 " ....          | 195                       | 0                        | —                          | Convulsions violent.    |
| " 9 " ....          | 166                       | —                        | —                          |                         |
| " 10 " ....         | 90                        | —                        | —                          | Blood pressure falling. |
| " 11 " ....         | 70                        | —                        | —                          |                         |



1903.]

*Action of the Poison of the Hyalrophidæ.*

TRACING I (1st HALF).

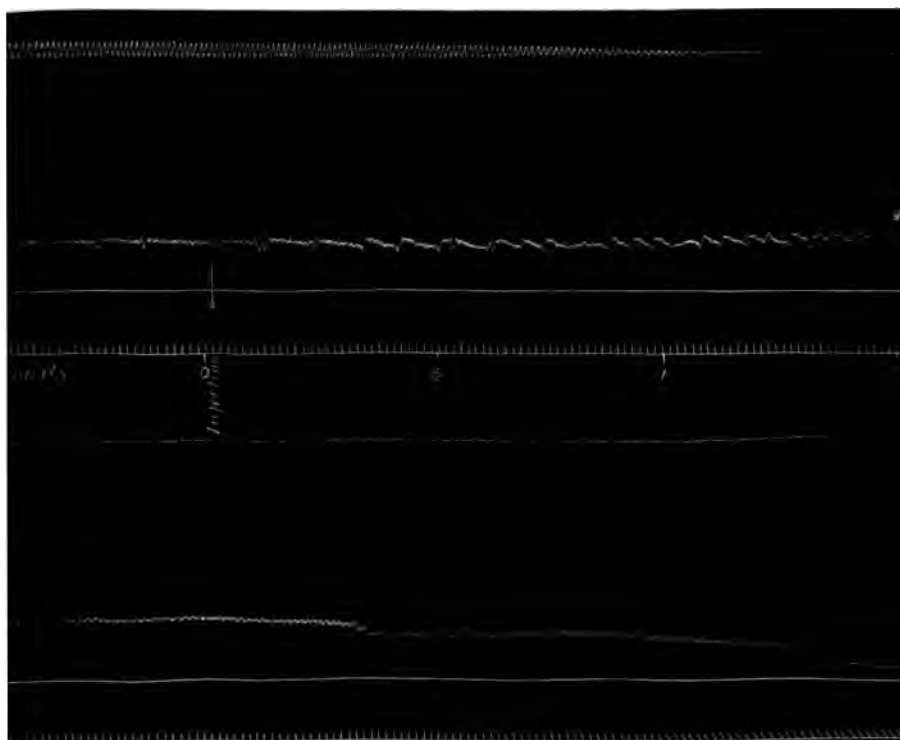


## Experiment 5.

Rabbit, weight 1·7 kilos., under chloroform. Conditions the same as in the above experiment, except that 6·8 milligrammes (4 milligrammes per kilo. weight) was given intravenously.

| Time.                         | Blood pressure in mm. Hg. | Respirations per $\frac{1}{4}$ minute. | Amplitude of respirations. | Remarks.                                       |
|-------------------------------|---------------------------|----------------------------------------|----------------------------|------------------------------------------------|
| Before injection ..           | 115                       | 43                                     | mm.<br>2                   |                                                |
| After $\frac{1}{4}$ min. .... | 115                       | 44                                     | 2                          |                                                |
| " 1 " ....                    | 115                       | 38                                     | 1                          |                                                |
| " $1\frac{1}{4}$ " ....       | 120                       | 32                                     | $\frac{1}{2}$              | Respiration failing.<br>Blood pressure rising. |
| " 2 " ....                    | 135                       | 22                                     | $\frac{1}{2}$              |                                                |
| " 3 " ....                    | 110                       | —                                      | —                          | Respiration ceased.                            |
| " $3\frac{1}{4}$ " ....       | 82                        | —                                      | —                          | Blood pressure falling.                        |

TRACING II.



Both the curves of the two experiments above detailed show the same sequence of results, viz., primary failure of respiration accompanied by a rise of blood pressure, followed by a fall of the same some little time after the respirations have entirely ceased. There is one remarkable and important difference between them, namely, an entire absence of respiratory convulsions in the case of the last very rapid poisoning. This absence of convulsions may be due to the respiratory centre being so rapidly overwhelmed by the relatively enormous dose of poison injected direct into the circulation (for the amount used amounted to some 200 times the minimal lethal dose for a rabbit), that the centre was paralysed completely before the failure of the breathing had had time to render the blood sufficiently venous to produce respiratory convulsions. The comparatively slight rise of blood pressure occurring with the failure in respiration in this case as compared with comparatively large rise obtaining in the other four experiments agrees with the explanation just suggested.

Another possible explanation must, however, be considered; a paralysis of the end plates of the motor nerves, which, as we shall see presently is a marked feature of the action of the poison under consideration, might cut off the peripheral muscles from the action of the respiratory centre, in spite of its over-stimulation by venous blood. In order to test this possibility, the right leg, exclusive of the sciatic nerve, was ligatured before the poison was injected in Experiment 5, and the response of the nerves and muscles of both limbs to the interrupted induced current was tested immediately after the death of the animal, with the following result:—

|                              | Distance of<br>secondary coil. | Contraction<br>of muscle. |
|------------------------------|--------------------------------|---------------------------|
| Protracted limb, nerve ..... | 45 mm.                         | Good.                     |
| "          muscle .....      | 45 "                           | Good.                     |
| Poisoned limb, nerve .....   | 0 "                            | Nil.                      |
| "          muscle .....      | 45 "                           | Good.                     |

Here we have a typical curara effect, the end plates of the poisoned limb only being completely paralysed. In this experiment it is therefore impossible to say how far the absence of convulsions is due to this cause and how far to failure of the respiratory centre. I shall return to this point further on, after the experiments on the action of the poison on the nerves have been related.

#### *Direct Action on the Heart.*

The next question to be dealt with is whether the poison of the *Enhydryna* has any direct action on the heart, which is so marked a feature in the case of *Pseudechis* poison,\* and has also been noted in

\* 'Roy. Soc. of New South Wales Proc.,' 1896.

a less marked degree by Brunton and Fayrer,\* when large doses of Cobra venom are introduced directly into the circulation. (In small doses, subcutaneously administered, Cobra venom has very little action on the heart, which can be kept going for many hours after spontaneous respiration has ceased by means of artificial respiration, as shown by the Indian Snake Poison Commission.)†

I have examined this point by testing if the poison has any paralysing action on the heart of a pithed frog, tracings being taken of the contraction of the organ before and after the direct action of solutions of the poison of various strengths in normal saline solution. As a few drops of a 1-in-1000 solution of Enhydrina poison given *per venam*, and therefore further greatly diluted in the circulation, is very rapidly fatal, it is evident that the poison should produce a very marked action on the heart when directly applied to it if the lethal effect is in any degree due to cardiac paralysis. My experiments have shown that such is not the case, for a 1-in-1000 solution when directly applied to a vigorous frog's heart produced no appreciable effect in any of several trials; a 1-in-100 solution, similarly applied on two occasions, did not retard, still less arrest the action of the heart.

#### *Effect of Artificial Respiration on the Blood Pressure and the Heart.*

The absence of any direct paralytic effect of Enhydrina poison on the heart was also shown by an experiment of another kind. As already mentioned, the heart can be kept going by artificial respiration for a very long time in Cobra poisoning, but this is not the case with poisoning with the venom of the *Pseudechis*; C. J. Martin‡ has shown that the heart fails within a very few minutes after cessation of spontaneous respiration, in spite of artificial respiration, in the case of the last-named snake poison, which also has a marked direct paralytic action on the heart. In the following experiment artificial respiration was started directly marked failure of respiration appeared and the blood pressure had begun to rise, and the effect of repeatedly stopping and recommencing it on the blood pressure was noted.

#### *Experiment 4.*

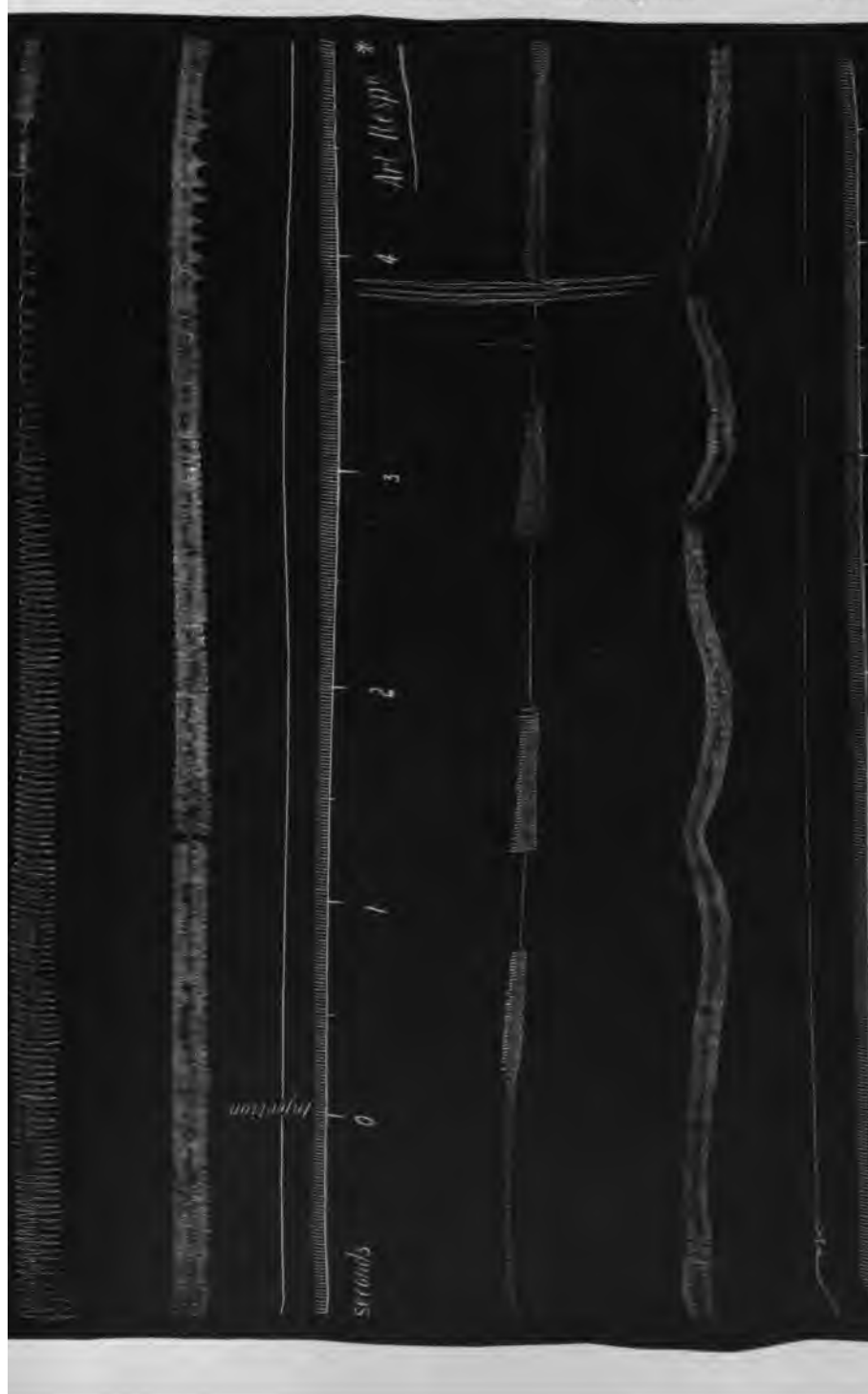
Cat, 3½ kilos., under chloroform. Cannula in the carotid artery, connected with a Gad's manometer. Respirations recorded with a Sandström's instrument. 7 milligrammes (2 milligrammes per kilo. weight) in 1.75 c.c. 0.9 per cent. NaCl injected into the jugular vein.

\* 'Roy. Soc. Proc.,' vols. 21, 22, and 23.

† 'Indian Medical Gazette,' 1873, p. 119.

‡ 'Roy. Soc. of New South Wales Proc.,' 1896.

| Time.            | Blood pressure. | Respirations. |            | Remarks.                                                                                             |
|------------------|-----------------|---------------|------------|------------------------------------------------------------------------------------------------------|
|                  |                 | No.           | Amplitude. |                                                                                                      |
| Before injection | Mm.             |               | Mm.        |                                                                                                      |
| After 1 min...   | 160             | 28            | 7          |                                                                                                      |
| " 2 " "          | 160             | 29            | 6½         |                                                                                                      |
| " 3 " "          | 160             | 27            | 5½         |                                                                                                      |
| " 4 " "          | 160             | 24            | 4          | Respirations beginning to fall.                                                                      |
| " 4 " "          | 170             | 16            | 2          | Blood pressure beginning to rise.                                                                    |
| " 4½ " "         | —               | —             | —          | Artificial respiration commenced.                                                                    |
| " 6½ " "         | 150             | —             | —          | Blood pressure fallen again.                                                                         |
| " 7½ " "         | 170             | —             | —          | Artificial respiration stopped.                                                                      |
| " 7½ " "         | 148             | —             | —          | Blood pressure risen again.                                                                          |
| " 8½ " "         | 180             | —             | —          | Artificial respiration resumed.                                                                      |
| " 9½ " "         | 150             | —             | —          | Blood pressure fallen again.                                                                         |
| " 9½ " "         | 185             | —             | —          | Artificial respiration stopped again.                                                                |
| " 11½ " "        | 140             | —             | —          | Blood pressure risen higher than previously; convulsions commencing. Artificial respiration resumed. |
| " 12½ " "        | 195             | —             | —          | Convulsions stopped; blood pressure fallen again. Artificial respiration stopped again.              |
| " 13½ " "        | 160             | —             | —          | Blood pressure risen, convulsions recommenced. Artificial respiration resumed.                       |
| " 15½ " "        | 198             | —             | —          | Convulsions stopped again; blood pressure fallen. Artificial respiration stopped.                    |
| " 18½ " "        | 140             | —             | —          | Blood pressure very high; feeble convulsions. Artificial respiration resumed.                        |
| " 21 " "         | 190             | —             | —          | Blood pressure fallen. Artificial respiration finally stopped.                                       |
| " 22½ " "        | 105             | —             | —          | Blood pressure high again, but no convulsions.                                                       |
| " 24 " "         | 70              | —             | —          | Final fall of blood pressure beginning.                                                              |



After the final failure of the circulation the sciatic nerves were tested with an interrupted induced current, and stimulation of both the nerves and the muscles directly caused contractions, showing that the smaller dose of poison used in this experiment had not caused paralysis of the end plates, although after the final cessation of artificial respiration no convulsions followed the rise in blood pressure. This points to complete exhaustion of the respiratory centre, occurring before paralysis of the end plates, having been the cause of the absence of terminal convulsions.

The repeated lowering of the blood pressure and disappearance of the commencing convulsions following immediately upon the performance of artificial respirations go to show that the rise of blood pressure and the convulsions are secondary in nature to the paralysis of the respiratory centre, and due to the increasing venosity of the blood. Further, it is evident that the poison has no powerful direct paralysing effect on the heart itself, as is the case with *Pseudechis* venom. The result of the above experiment is also of interest in connection with one by Vincent Richards,\* in which a dog was bitten by an *Enhydrina*, and artificial respiration was kept up for 24 hours and 35 minutes after the failure of respiration, sensibility being restored, and at the same time convulsions recurred, pointing to partial recovery of the respiratory centre from the condition of complete paralysis. Death finally occurred by accidental arrest of artificial respiration. In his experiment the dose given was a small one, as respiration did not cease until after two hours, but it is evident that the poison exerted no injurious action on the heart.

#### *Action on Nerves and End-Plates.*

Brunton and Fayrer† first showed that Cobra venom exerts a paralysing action on the muscles' end-plates like curara; this was confirmed by Ragotzi,‡ and the last-mentioned observer attributed the failure of respiration to paralysis of the end-plates of the diaphragm. We have already seen (Experiment 5) that a similar motor nerve paralysis may result from *Enhydrina* poisoning, so that it is necessary to inquire whether this is due to an effect on the nerve trunk or on the end-plates. If the nerve trunk is itself poisoned, so as to lose its power of conductivity, then the negative variation of the current of injury should be greatly reduced or entirely abolished by very dilute solutions of the venom. This has been tested by Dr. Waller's method by placing the sciatic nerves of frogs in dilute solutions of the venom, and measuring the negative variation of the current of injury with a galvanometer both before and after exposure to the poison. The nerves were first

\* 'Indian Medical Gazette,' 1873, p. 119.

† 'Roy. Soc. Proc.,' vols. 21, 22, and 23.

‡ 'Virchow's Archiv,' vol. 122, p. 232.

placed in 0·83 per cent. NaCl for about two hours, this strength having been found recently by Dr. N. H. Alcock (to whom I am indebted for much help throughout this investigation) to be the optimum one for nerves.

The poison was used in strengths of from  $10^{-6}$  to  $10^{-8}$ , and the nerves were exposed to their influence for from 1—5 minutes in the case of the stronger solutions, and up to 1 hour in the weaker one, but with entirely negative results. In one experiment a 1 per cent. solution was used up to 5 minutes without any poisonous effect on the nerve being produced, although this is a stronger solution than I have ever used for injection. It is evident, then, that the poison of the *Enhydrina* does not produce paralysis by any direct action on the nerve fibres.

That it does act by paralysing the muscle end-plates, as in the case of Cobra venom, is shown by the following experiments on etherised frogs.

Frog. Weight 20 grammes. Etherised. Right thigh ligatured, excluding the sciatic nerve. 0·2 milligramme Enhydrina poison in 0·2 c.c. 0·9 per cent. NaCl injected into dorsal lymph sac. (10 milligrammes per kilo. = 20 minimal lethal doses.)

Respirations per minute.

|                        |    |               |    |
|------------------------|----|---------------|----|
| Before injection ..... | 56 | 5th min. .... | 19 |
| 1st min. ....          | 68 | 6th „ ....    | 5  |
| 2nd „ ....             | 64 | 7th „ ....    | 9  |
| 3rd „ ....             | 50 | 8th „ ....    | 0  |
| 4th „ ....             | 32 | 9th „ ....    | 0  |

Respirations finally ceased. Heart still beating 4 hours later. After cessation of respiration the frog was pithed, and when the spinal cord was destroyed, the ligatured (protected) limb only showed contraction of the muscles. Both the sciatic nerves and leg muscles were then tested with the interrupted faradic current, with the following results:—

|                             | Distance of<br>secondary coil. | Contraction<br>of muscle. |
|-----------------------------|--------------------------------|---------------------------|
| Protected limb, nerve ..... | 40 mm.                         | Good.                     |
| „ muscle .....              | 30 „                           | Good.                     |
| Poisoned limb, nerve .....  | 0 „                            | Nil.                      |
| „ muscle .....              | 30 „                           | Good.                     |

This is a typical curara effect, and on proceeding to test the negative variation of the current of injury of the sciatic nerves of each limb, after placing them in 0·83 per cent. NaCl for 2 hours, both nerves were found to give it well, that of the poisoned limb being slightly the stronger of the two, probably owing to partial drying of that of the protected limb over the ligature.

The above experiment was repeated with a dose of 5 milligrammes



per kilo. weight, with a precisely similar result, including the presence of the negative variation of the current of injury in each sciatic nerve. In two more experiments doses of 5 and 1 milligrammes per kilo. respectively were injected without previous ligaturing of a limb, and in both cases stimulation of the nerves of each limb caused no muscle response, although they contracted when directly stimulated. In each case both nerves showed well-marked negative variation of the current of injury, proving that their conducting powers were intact, so that it is clear that the end-plates must have been paralysed.

*Action on the End-Plates of the Phrenic Nerves.*

The marked action on the motor end-plates of the poison of the Enhydrina once more brings it into line with that of Cobra venom, but on the other hand constitutes a marked difference from Pseudechis venom, which C. J. Martin showed had no such action. He also found that the stimulation of the phrenic nerves still produced normal contraction of the diaphragm after total cessation of respiration due to the latter poison.

In order to ascertain how far the paralysis of respiration produced by Enhydrina venom is due to paralysis of the respiratory centre, and how far, if at all, to poisoning of the motor end-plates of the phrenic nerves, the following experiments were performed.

Cat, weight  $3\frac{1}{2}$  kilos., under chloroform. Tracheal cannula connected with a recorder inserted. Left phrenic nerve exposed in the neck,  $3\frac{1}{2}$  milligrammes of Enhydrina poison injected into external jugular vein (1 milligramme per kilo.). Phrenic nerve stimulated by an interrupted induced current at intervals of one minute.

Occasional feeble inspirations produced by movement of the chest walls only, continued up to the 24th minute, when they finally ceased. At the 27th minute the final rapid fall of blood pressure to 50 mm. took place. The sciatic nerves were tested at this point, and the right when stimulated with the secondary coil at 30 mm. produced a good muscular response, as did the left with the secondary coil at  $27\frac{1}{2}$  mm. It appears from this that the phrenic nerve was paralysed completely before any very marked loss of function of the sciatic nerves had taken place. The respirations, however, were very greatly reduced in both frequency and amplitude several minutes before any weakening of the phrenics had occurred, so that the first and most important action of the poison appears to be its effect on the respiratory centre, although the paralysis of the phrenics speedily ensues and is a very important feature of the action of the venom. If a very large dose is given, as in Experiment 5, then the end-plates of the muscles in general are also paralysed at the same time or very soon after the failure of the respiratory centre and the phrenics.

| Time.               | Blood pressure. | Respirations per minute. | Phrenic nerve. |                           | Remarks.                                               |
|---------------------|-----------------|--------------------------|----------------|---------------------------|--------------------------------------------------------|
|                     |                 |                          | Coil at        | Contraction of diaphragm. |                                                        |
| Before injection... | mm.             | 45                       | 25 mm. only    | Good.                     |                                                        |
| After 3 min.        | 150             | 41                       | "              | "                         |                                                        |
| " 6 "               | 165             | 33                       | "              | "                         |                                                        |
| " 9 "               | 169             | 17                       | "              | "                         |                                                        |
| " 12 "              | 170             | 10                       | "              | Slight.                   |                                                        |
| " 14 "              | 170             | 8                        | "              | Nil.                      |                                                        |
| " 16 "              | 150             | 3                        | 20             | Slight.                   |                                                        |
|                     |                 |                          | 20             | Nil.                      | Respirations nearly ceased, phrenics weakened.         |
| " 17 "              | 100             | Convulsions              | 15             | Slight.                   |                                                        |
|                     |                 |                          | 15             | Nil.                      |                                                        |
| " 19 "              | 100             | Do.                      | 10             | Good.                     |                                                        |
|                     |                 |                          | 0              | Nil.                      | Phrenics completely paralysed. Blood pressure falling. |

The above experiment was repeated in a rabbit, with a precisely similar result to that just detailed, the respiratory centre failing first, quickly followed by paralysis of the phrenics, although the diaphragm still responded to direct excitation. The muscles of both limbs (one of which was ligatured before the injection of the poison) contracted well immediately after death to both direct stimulation and that through the sciatic nerves. In this experiment the respirations failed very rapidly, ceasing at the end of two minutes, and no convulsions ensued, in spite of the motor end-plates not being paralysed, so that in this instance the absence of convulsions could not be due to muscular paralysis, but only to complete paralysis of the respiratory centre.

#### *Action of the Spinal Cord Reflexes.*

In the case of Cobra poisoning Brunton and Fayrer showed that the spinal cord is paralysed from below upwards, the hind legs being first affected. C. J. Martin also found that a direct poisonous action on the spinal cord was produced by *Pseudechis* venom.

In order to test this point a frog was etherised, and after a ligature had been tied round the right thigh, excluding the sciatic nerve, a dose of 5 milligrammes per kilo. of *Enhydrina* poison was injected into the dorsal lymph sac, and the reflexes induced by stimulating the skin of different parts of the body with an interrupted induced current with

the secondary coil at 5 mm. were observed. Respiration finally ceased at the end of 40 minutes. The sequence of events as regards reflexes was as follows: During the first 25 minutes, stimulation of the left foot produced contractions in both the legs and arms, as did also stimulation of either arm, showing that the reflexes were intact. After 27½ minutes, stimulation of the left foot still produced good movement in the arms, as well as in the legs, but stimulation of an arm now produced only a feeble movement of the legs. After 35 minutes, stimulation of the left leg produced only feeble movement in it, although the right (protected) limb still responded well, the motor end plates in the poisoned limb being now partially paralysed. Stimulation of one arm now produced no movement of the poisoned leg, but both arms contracted well. After 40 minutes, in addition to the conditions just noted, it was found that when the current was applied to the eye directly, movement occurred in all four limbs, showing that a powerful stimulus still produced a cord reflex. When, however, the current was applied over the lower end of the vertebral column, the legs only contracted, and when applied over the dorsal region the arms only moved, showing some impairment of the functions of the spinal cord so far as conduction in its long axis was concerned. On stimulating one arm, however, both upper limbs contracted, showing conduction transversely in the upper part of the cord still persisted. After 45 minutes the transverse conduction had also disappeared, for stimulation of one upper extremity only caused contraction of the irritated limb, and not of the opposite one, although when the electrodes were placed over the upper cord itself both limbs responded. On applying the electrodes to the eye directly at this stage, the protected limb contracted well, and the three poisoned ones feebly only, while 7½ minutes later this powerful stimulus produced a reflex action of a very feeble nature in the protected leg only. The heart was still beating, but respiration had ceased for some minutes, the animal being quite flaccid, and apparently dead; the nerve trunks of the limbs were now exposed, and stimulated directly, to ascertain how far the end-plates were paralysed, with the following results: The muscles of all four limbs still responded to direct stimulation. The sciatic nerve of the left (poisoned limb) gave no response at all with the secondary coil at 0. That of the right (protected limb) responded with the coil at 15 mm. On testing the arm nerves, contractions were produced with the coil at 7½ mm., but not at 10 mm., showing only partial paralysis of the end plates of the arm muscles at a time when those of the poisoned lower limb were completely paralysed; an important point, which must be taken into account in considering how far the changes in the reflexes detailed above can be taken as evidence of loss of function of the spinal cord, as apart from the affection of the motor end-plates. The loss of the transverse reflex in the upper cord when the motor end

plates of the muscles of the upper extremities were not paralysed, points to a diminution of the reflex functions of the spinal cord. On the other hand, the marked reflex contraction of all four limbs on applying a strong current to the eye just after respiration had ceased, shows that the reflex functions of the cord were not abolished at this period, although they rapidly declined within a few minutes of complete respiratory paralysis, as would be expected. The less rapid affection of the motor end-plates of the upper extremity, as compared with those of the lower limbs, accounts for the ascending paralysis apart from any interference with the functions of the spinal cord itself.

We must conclude, then, that the respiratory paralysis is complete before the reflex functions of the spinal cord are abolished, although they may be diminished at an earlier stage, so that the action of Enhydrina poison on the spinal cord itself is of quite secondary importance as compared with the paralysis of the respiration and of the motor end-plates of the muscles.

#### *Conclusions.*

1. In lethal doses, Enhydrina poison has no direct depressing action on the heart. The marked rise in blood pressure observed is secondary to failure of respiration, producing venosity of the blood.

2. The primary action of the poison is the production of a respiratory paralysis by a direct action on the respiratory centre, this being very quickly followed by paralysis of the end-plates of the phrenic nerves. The latter may occur at a time when the sciatic nerves show no end plate paralysis.

3. The poison has a very marked action in paralysing the end-plates of motor nerves, but does not perceptibly affect the conducting powers of the nerve trunks themselves. In this respect it resembles Cobra venom and curara.

4. Its action on the reflex functions of the spinal cord is slight, and altogether secondary in importance to its influence on respiration.

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"The Action of Choline, Neurine, Muscarine, and Betaïne on Isolated Nerve and upon the Excised Heart." By A. D. WALLER, M.D., F.R.S., and S. C. M. SOWTON. Received June 12,—Read June 18, 1903.

In connection with the identification by Halliburton and Mott of choline in morbid cerebro-spinal fluid, we compared the action upon isolated nerve and upon the excised heart of the four closely related organic bases: choline,  $C_5H_{15}NO_2$ ; neurine,  $C_5H_{13}NO$ ; muscarine,  $C_5H_{13}NO_2$ ; and betaine,  $C_5H_{13}NO_3$ ; we have also, thanks to the kindness of Professor Wright and of Mr. Plimmer, taken occasion to examine in a similar manner certain pathogenic toxines, viz.: snake venom (Calmette), diphtheria toxin, and tetano-toxin.

According to previous investigators, muscarine is powerfully toxic, arresting the heart in diastole (Schmiedeberg); neurine has an action resembling that of muscarine; choline (which formerly was not distinguished from neurine) has a less powerful action than that of neurine, and betaine is considered to be an inert substance. (With regard to their possible action upon nerve, there are, so far as we know, no definite observations.) The direct action of muscarine upon nerve was incidentally examined by one of us in a general survey of the action upon nerve of a series of vegetable alkaloids; that of choline and neurine was examined in comparison with a cerebro-spinal residue and briefly reported upon at the Cambridge Congress of Physiology (1897).

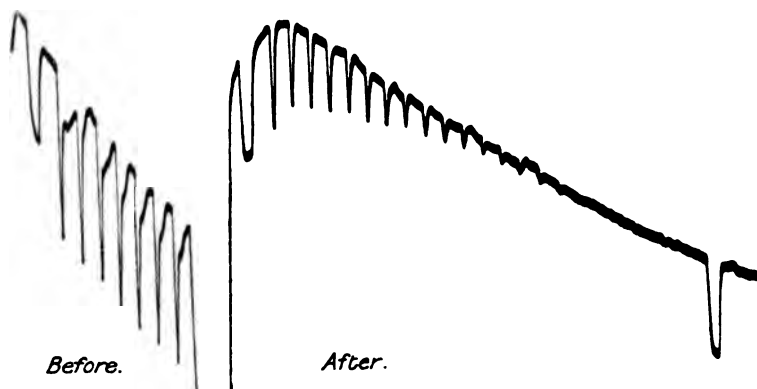
At that time, confining ourselves to a procedure in which the nerve was submitted to observation for a period not exceeding one hour, interrupted by a period of immersion of one minute duration, we found that muscarine was to be ranked with alkaloids possessing "little or no action" upon nerve, with, however, the express reservation that "such a statement must not be taken as committing us to a denial of any action whatever by the drug acting in stronger solution or for a longer period."

And in point of fact, muscarine which, under the conditions systematically observed by us at the outset of these observations, is to be classified as inactive, is manifestly active (*a*) in stronger solution for the same short period of immersion, and (*b*) in the same weak solution for a longer period of immersion. The former of these two statements is illustrated by fig. 1 (3319), giving the effect of muscarine nitrate in 10-per cent. solution acting for one minute; the latter statement by *e.g.*, fig. 4 (*vide infra*), which represents the course of an observation extending over 60 hours, in which two nerves were three times submitted to prolonged immersion in a 1-per cent. solution of *muscarine hydrochloride*.

As regards choline, neurine, and the cerebro-spinal residue our report of a summary examination of these three bodies was to the effect that choline as compared with neurine was inert, that cerebro-spinal residue was inert while fresh, but became active when oxidised, and that "as regards an action upon isolated nerve the order of efficacy of the samples in our possession was (1) neurine, (2) muscarine, (3) choline."\*

This result, although accurate for the particular samples in our hands, was, however, vitiated by an error in their description. The so-called "neurine hydrochloride" of our first experiments

FIG. 1 (Muscarine nitrate).



3313 to 3317, was in reality the base neurine, which in 25-per cent. solution has a basic reaction requiring for its neutralisation 2 vols. of normal acid. The effects of 4, 2, 1, and  $\frac{1}{2}$  and  $\frac{1}{4}$  per cent. solutions of neurine are, therefore, partly or wholly basic effects by 0.32, 0.16, 0.08, 0.04, and 0.02 solutions of normal alkali. These effects were in fact such as we are accustomed to expect from other basic solutions such as potash or soda, of strength ranging from 0.20 to 0.05 normal (acid and alkali).

A strict comparison between the two bodies requires the use of both bodies as bases, neither of which conditions we have yet found means to fulfil. For, on the one hand, neurine when neutralised by an acid (*e.g.*, hydrochloric), is decomposed to an ammonium salt, etc., on the other, choline as base is extremely unstable.

A fresh series of experiments for determining the relative effects of choline and neurine upon isolated nerve was made in the summer of 1900. We obtained from Messrs. Merck the four

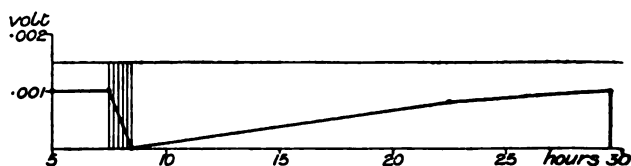
\* Sowton and Waller, Internat. Physiol. Congress, Cambridge, 1898, 'Journ. of Physiol.,' vol. 23, suppl., p. 35.

substances: choline and neurine pure, choline hydrochloride, and neurine hydrochloride. These were used in solutions of 10 per cent. or less, and in the case of the pure substances both unneutralised and neutralised solutions were tried. Series of nerves were immersed (a) for 1 minute, (b) for 30 minutes, the experiments being photographically recorded. At the end of each experiment the nerve was replaced in physiological saline, and some hours later, usually the next morning, having received a new transverse section, it was again tested in order to ascertain whether any effect that had been recorded was permanent or merely temporary.

In making up solutions of choline the question arose as to whether physiological saline or distilled water should be used. Saline being inadmissible in the case of neurine, the comparisons to be made would be more fair, it seemed, if all solutions were made with distilled water.

In working, however, with choline hydrochloride, a solution was made up with saline, and a second one with distilled water, in order by comparing the effects of the two, to estimate roughly what proportion of any effect obtained should be attributed to the action of the distilled water. In the course of former experiments some attention had already been paid to the separate action of distilled water upon nerve, and immersion for 30 minutes was found to diminish its electromobility. But between the two choline hydrochloride

FIG. 2.—Distilled water.



solutions no great difference of effect could be noticed. After this first trial the solutions of both choline and neurine were made up with distilled water only.

A 1-minute bath of choline hydrochloride at 10 per cent. has little or no effect upon nerve response. A 30-minute bath of the same solution diminishes the deflection, but soakage for some hours in physiological saline restores completely the electromobility of the nerve. The drug then may be said to be active in strong solutions applied for a considerable time—it cannot be characterised as “toxic.”

With neurine hydrochloride in 10 per cent. solution the effect of a 1-minute bath is diminution of the electromobility of the nerve, similar in degree to that observed after 30 minutes of choline hydrochloride of the same strength, but the nerve treated with neurine gives after

Table A.—Choline Hydrochloride

| No. of plate.                                                                                                                                                                                                                                                         | Substance.                        | Solution.                   | Time.      | Remarks.                                                                                      |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------|-----------------------------|------------|-----------------------------------------------------------------------------------------------|
| 3601                                                                                                                                                                                                                                                                  | Choline hydrochloride .....       | 10 p. c. in distilled water | mins.<br>1 | No diminution of response.                                                                    |
| 3602                                                                                                                                                                                                                                                                  | " .....                           | " saline .....              | 1          | Little or no effect.                                                                          |
| 3603                                                                                                                                                                                                                                                                  | " 2nd bath ....                   | " distilled water           | 30         | Diminution by 0.00023 volt in 20 mins. (0.00098 to 0.00065 volt) (nerve of 3601).             |
| 3604                                                                                                                                                                                                                                                                  | " .....                           | " "                         | 1          | Little or no effect.                                                                          |
| 3605                                                                                                                                                                                                                                                                  | " .....                           | " "                         | 1          | Little or no effect.                                                                          |
| 3606                                                                                                                                                                                                                                                                  | " 2nd bath ....                   | " "                         | 20         | Marked diminution, by 0.00054 volt within 20 mins. (0.00075 to 0.00021 volt) (nerve of 3604). |
| 3607                                                                                                                                                                                                                                                                  | " .....                           | " saline .....              | 30         | Diminution to trace within 20 mins.                                                           |
| 3608                                                                                                                                                                                                                                                                  | " .....                           | " "                         | 30         | Diminution by 0.00021 volt within 20 mins. (0.00034 to 0.00033 volt).                         |
| 3609                                                                                                                                                                                                                                                                  | " 2nd bath ....                   | " distilled water           | 30         | Diminution by 0.00036 volt within 20 mins. (0.00058 to 0.00022 volt).                         |
| The effect, where effect was observed, was in these cases gradual. Two experiments made when the solution was five or six weeks old, show more rapid action, but in these cases also the effect was only temporary, both nerves giving good deflections the next day. |                                   |                             |            |                                                                                               |
| 3679                                                                                                                                                                                                                                                                  | Choline hydrochloride (old) ..... | 10 p. c. in distilled water | 30         | Abolition of response.                                                                        |
| 3680                                                                                                                                                                                                                                                                  | " .....                           | " "                         | 30         | Trace left, abolition complete within 6 mins.                                                 |



Table B.—Neurine Hydrochloride.

| No. of plate. | Substance.                  | Solution. | Time.      | Remarks.                                                                                                         |
|---------------|-----------------------------|-----------|------------|------------------------------------------------------------------------------------------------------------------|
| 3645          | Neurine hydrochlorine ..... | 10 p. c.  | mins.<br>1 | Diminution by 0.00108 volt within 25 mins. (0.0018 to 0.00072 volt).                                             |
| 3646          | " .....                     | "         | 1          | Little or no effect.                                                                                             |
| 3647          | " 2nd bath .....            | "         | 30         | Abolition complete and final (nerve of 3645).                                                                    |
| 3648          | " " .....                   | "         | 30         | Abolition complete and final (nerve of 3646).                                                                    |
| 3649          | " .....                     | "         | 1          | Marked diminution, by 0.00048 volt within 25 mins. (0.00066 to 0.0002 volt).                                     |
| 3650          | " .....                     | "         | 30         | Trace for first few minutes after bath, then final abolition.                                                    |
| 3651          | " .....                     | "         | 1          | Diminution, by about 0.0005 volt within 25 mins. (0.001 to about 0.0005 volt). Deflection just visible next day. |
| 3652          | " .....                     | "         | 1          | Diminution marked, 0.0009 volt within 20 mins. (0.001 to 0.001 volt). No response next day.                      |
| 3653*         | " .....                     | "         | 1          | Augmentation by 0.00033 volt (0.00043 to 0.00074 volt). Good deflection next day.                                |
| 3654          | " .....                     | "         | 1          | Diminution by 0.00041 volt within 25 mins. (0.00078 to 0.00037 volt). Very small deflection next day.            |
| 3655          | " .....                     | "         | 1          | Diminution by 0.0005 volt within 25 mins. (0.008 to 0.0003 volt). No response next day.                          |
| 3656          | " .....                     | "         | 30         | Abolition, complete and final.                                                                                   |
| 3657          | " .....                     | "         | 30         | Diminution to a trace within 25 mins. No recovery.                                                               |
| 3658          | " .....                     | "         | 30         | Abolition, complete and final.                                                                                   |

long soaking in physiological saline either a much-reduced deflection or none at all. One exceptional case was recorded: on Plate 3653, the effect of neurine hydrochloride for 1 minute is marked augmentation, and the nerve on being tested the next day gave a good deflection.

With a 30-minute bath of neurine hydrochloride the effect is usually abolition immediate and final. In two cases a very small deflection was recorded after the bath (Plates 3650, 3657), but in no case was there any subsequent recovery.

Pure choline, giving an alkaline reaction, was first tested in its non-neutralised state. Immersion of the nerves for 1 minute had always some effect, though not a marked one. Out of six records taken, three show slight diminution, the other three slight augmentation. Four of the nerves were tested the next day and gave deflections, three of them large ones. The two other nerves were subjected the same day to the longer bath—30 minutes—with the result recorded on plates 3666, 3667, viz., diminution to a mere trace within 20 minutes and abolition within 12 minutes; both, however, gave small deflections on being tested the following day. In three other experiments with a bath of 30 minutes the deflection was reduced, markedly in two cases—but there was partial recovery by the next day. In the remaining case the diminution was less marked on the record, but there was no after recovery.

To obtain a 10-per cent. neutralised solution of choline, 1 vol. 20 per cent. choline was mixed with 1 vol. sulphuric acid  $n/10$ . The effect upon nerve was less marked than in the case of pure choline solution, which had shown one example of final abolition; the neutralised solution gave, for the most part, diminution, but the recovery was apparently more complete than with pure choline. In one experiment (3672) the deflection next day was very small.

Pure neurine non-neutralised was found as in former experiments to be very toxic to nerve. At 10, 8, 5, and 4 per cent., immersion for 1 minute abolished all response. (The one exceptional case recorded, Plate 3612, where the effect was only slight diminution, we cannot attempt to explain; at 2 per cent.—1 minute bath—the deflection was abolished, but there was partial recovery by the next day.) At 1 per cent.—1 minute—there was diminution or abolition with recovery.

The results obtained with neutralised neurine were not very satisfactory. The neurine was received from Messrs. Merck in a 25-per cent. solution and required for the neutralisation 2 vols of normal sulphuric acid. A glance at the table of experiments will show how uncertain are the effects as compared with those of neurine hydrochloride. For instance, Nos. 3619 and 3620 were a pair of nerves subjected to a 1-minute bath of 8 per cent. neutralised neurine; there was little or no effect upon either nerve, they were then further

Table C.—Choline (Alkaline).

| No. of plate. | Substance.               | Solution. | Time.      | Remarks.                                                                                         |
|---------------|--------------------------|-----------|------------|--------------------------------------------------------------------------------------------------|
| 3650          | Choline, not neutralised | 10 p. c.  | mins.<br>1 | Diminution by 0.00038 volt within 28 mins. (0.00067 to 0.00059 volt). Small deflection next day. |
| 3660          | "                        | "         | 1          | Diminution by 0.00024 volt within 20 mins. (0.00077 to 0.00053 volt) Good deflection next day.   |
| 3661          | "                        | "         | 30         | Marked diminution by 0.00098 volt within 20 mins. (0.0011 to 0.00012 volt). Deflection next day. |
| 3662          | "                        | "         | 1          | Augmentation by 0.0003 volt (0.0007 to 0.001 volt). Nerve used again.                            |
| 3663          | "                        | "         | 1          | Augmentation by 0.00028 volt (0.00068 to 0.00095 volt). Nerve used again.                        |
| 3664          | "                        | "         | 1          | Diminution by 0.00012 volt (0.00075 to 0.00063 volt). Good deflection next day.                  |
| 3665          | "                        | "         | 1          | Augmentation by 0.00014 volt (0.00089 to 0.00103 volt). Good deflection next day.                |
| 3666          | "                        | 2nd bath  | 30         | Diminution to trace within 20 mins. Small deflection next day (nerve of 3663).                   |
| 3667          | "                        | "         | 30         | Abolition within 12 mins. Deflection next day (nerve of 3663).                                   |
| 3668          | "                        | "         | 30         | Diminution by 0.00088 volt within 20 mins. (0.00095 to 0.00057 volt). Small deflection next day. |
| 3669          | "                        | "         | 30         | Marked diminution by 0.00052 volt (0.0007 to 0.00018 volt). No deflection next day.              |

Table C—*continued.*

| No. of plate. | Substance.                 | Solution. | Time.      | Remarks.                                                                                                             |
|---------------|----------------------------|-----------|------------|----------------------------------------------------------------------------------------------------------------------|
| 3670          | Choline, neutralised ..... | 10 p. c.  | mins.<br>1 | Slight augmentation by 0·0001 volt (0·0006 to 0·0007 volt).<br>Good deflection next day.                             |
| 3671          | " .....                    | "         | 1          | Diminution by 0·00014 volt (0·00075 to 0·00061 volt). Good deflection next day.                                      |
| 3672          | " .....                    | "         | 30         | Primary augmentation, no diminution on plate, but very small deflection next day.                                    |
| 3673          | " .....                    | "         | 30         | Diminution to a trace within 20 mins. Good deflection next day.                                                      |
| 3674          | " .....                    | "         | 30         | Primary augmentation. Good deflection next day.                                                                      |
| 3675          | " .....                    | "         | 30         | Primary augmentation, then diminution by 0·0008 volt within 20 mins. Not tested next day.                            |
| 3676          | " .....                    | "         | 30         | Diminution by 0·0007 volt within 20 mins. (0·0025 to 0·0018 volt). Not tested next day.                              |
| 3677          | " .....                    | "         | 30         | Diminution. Good deflection next day.                                                                                |
| 3678          | " .....                    | "         | 30         | Diminution. Good deflection next day.                                                                                |
| 3681          | " .....                    | "         | 1          | Augmentation by 0·0004 volt (0·001 to 0·0014 volt).                                                                  |
| 3682          | " .....                    | "         | 1          | Slight augmentation by 0·0001 volt (0·0017 to 0·0018 volt).<br>Good deflection next day (nerve used on 3683).        |
| 3683          | " .....                    | "         | 30         | Diminution by 0·00084 volt (0·00124 to 0·0006 volt) within 20 mins. Very small deflection 8 hrs. later and next day. |
| 3684          | " .....                    | "         | 30         | Abolition within 20 mins. Deflection next day.                                                                       |
| 3685          | " .....                    | "         | 30         | Diminution by 0·00051 volt within 20 mins. (0·00089 to 0·00038 volt). Deflection next day.                           |

Table D.—Neurine (Alkaline).

| No. of plate. | Substance.               | Solution. | Time.<br>mins. | Remarks.                                             |
|---------------|--------------------------|-----------|----------------|------------------------------------------------------|
| 3610          | Neurine, not neutralised | 10 p. c.  | 1              | Abolition immediate and final.                       |
| 3611          | "                        | "         | 1              | Ditto.                                               |
| 3629          | "                        | 8 p. c.   | 1              | Ditto.                                               |
| 3630          | "                        | "         | 1              | Ditto.                                               |
| 3612*         | "                        | 5 p. c.   | 1              | Slight diminution. Not tested again.                 |
| 3613          | "                        | "         | 1              | Abolition immediate and final.                       |
| 3638          | "                        | "         | 1              | Ditto.                                               |
| 3641          | "                        | 4 p. c.   | 1              | Ditto.                                               |
| 3642          | "                        | "         | 1              | Ditto.                                               |
| 3643          | "                        | 2 p. c.   | 1              | Abolition within 15 mins. Small deflection next day. |
| 3644          | "                        | "         | 1              | Abolition within 15 mins. Small deflection next day. |
| 3639          | "                        | 1 p. c.   | 1              | Abolition within 10 mins. Good deflection next day.  |
| 3640          | "                        | "         | 1              | Diminution. Deflection next day.                     |

Table D—*continued.*

| No. of plate. | Substance.                 | Solution.          | Time.      | Remarks.                                                                                                |
|---------------|----------------------------|--------------------|------------|---------------------------------------------------------------------------------------------------------|
| 3614          | Neurine, neutralised ..... | 5 p. c.            | mins.<br>1 | Little or no effect. The nerve was afterwards submitted to non-neut. 5 p. c. solution, which killed it. |
| 3615          | " .....                    | 8 p. c.<br>(about) | 1          | Diminution by 0.001 volt within 25 mins. (0.002 to 0.001 volt).                                         |
| 3616          | " .....                    | "                  | 1          | Diminution by 0.0011 volt (0.00083 to 0.00022 volt).                                                    |
| 3617          | " .....                    | "                  | 30         | Immediate abolition. But gives deflection next day.                                                     |
| 3618          | " .....                    | "                  | 30         | Immediate abolition.                                                                                    |
| 3619          | " .....                    | "                  | 1          | Little or no effect. Nerve used again, pl. 3621.                                                        |
| 3620          | " .....                    | "                  | 1          | Little or no effect. Nerve used again, pl. 3622.                                                        |
| 3621          | " .. 2nd bath .....        | "                  | 30         | Diminution by 0.0005 volt within 20 mins. (0.001 to 0.0005 volt).                                       |
| 3622          | " " .....                  | "                  | 30         | Good deflection next day.<br>Abolition within 5 mins. No recovery.                                      |
| 3623          | " .....                    | "                  | 30         | Abolition immediate and final.                                                                          |
| 3624          | " .....                    | "                  | 30         | Ditto.                                                                                                  |
| 3625          | " .....                    | 4 p. c.<br>(about) | 30         | Very slight increase on record. No deflection next day.                                                 |
| 3626          | " .....                    | "                  | 30         | Diminution by 0.0005 volt within 25 mins. (0.0015 to 0.001 volt).                                       |
| 3627          | " .....                    | "                  | 30         | Slight augmentation. Deflection next day.                                                               |

Table D—*continued*

| No. of plate. | Subject.                   | Solution.          | Time. | Remarks.                                                                                              |
|---------------|----------------------------|--------------------|-------|-------------------------------------------------------------------------------------------------------|
| 3628          | Neurine, neutralised ..... |                    | mins. |                                                                                                       |
| 3631          | " .....                    | 4 p. c.<br>(about) | 30    | Slight augmentation. Deflection next day.                                                             |
| 3632          | " .....                    | 2 p. c.            | 30    | Slight augmentation. No deflection next day.                                                          |
| 3633          | " .....                    | "                  | 30    | No effect. Small deflection next day.                                                                 |
| 3634          | " .....                    | "                  | 30    | Diminution by 0.0006 volt within 20 mins. (0.00082 to 0.00022 volt). No deflection next day.          |
| 3635          | " .....                    | "                  | 30    | Diminution by 0.0006 volt within 20 mins. (0.0013 to 0.0008 volt). Deflection first visible next day. |
| 3636          | " .....                    | "                  | 30    | Slight augmentation followed by slight diminution. Good deflection next day.                          |
|               | " .....                    | "                  | 30    | Slight diminution. Good deflection next day.                                                          |

immersed for 30 minutes in the same solution, with the result, in the first case, of diminution followed by recovery, in the second case, of abolition with no subsequent recovery. In 3617 the 30-minute bath was of the same strength as before, its effect was immediate abolition, but the nerve gave a deflection the next morning. In 3623 there was also immediate abolition, but in this case it was final. Nos. 3625 and 3627 may also be contrasted, in each case 30 minutes immersion in a 4-per cent. solution produced a slight augmentation of response, but tested the next morning the one gave a deflection and the other none. It would appear, therefore, that neurine hydrochloride is much more suitable for such experiments as these than neutralised neurine. We should mention that the frogs were in bad condition at the time these experiments were made, the weather being very hot. But this element of uncertainty would not alone account for the marked inequalities noticed.

*Betaine Hydrochloride.*—We made use of two samples of this substance, one coming from Merck's factory, the other from the laboratory of Professor Boehm. The salt in each case when dissolved in 10-per cent. solution in normal saline had a strongly acid reaction, requiring for neutralisation half its volume of normal soda solution.

The effects of unneutralised solutions at 10, 5, 4, 2, and 1 per cent. are therefore partly or wholly acidic effects by 0.50, 0.25, 0.20, 0.10, 0.05 solutions of normal acid. We did not, however, work with these, but with neutralised solutions.

*Method.* Nerve.—The excised sciatic nerve of frog, kept not longer than 24 hours in physiological saline, is laid across two pairs of unpolarisable electrodes in a moist chamber. The normal excitatory effect (negative variation) is observed, preferably after as well as before the cut end of the nerve has been refreshed by a new transverse section. The nerve is then put to soak in the experimental solution, and from time to time replaced upon the electrodes to be tested as before. If, and when the excitatory effect is abolished, both before and after a fresh transverse section, the nerve is put to soak in physiological saline, and from time to time tested as before for a possible recovery of electromobility.

Proceeding thus we are enabled to qualify any given solution as being: 1° inert or weak, 2° moderately active, 3° strong according as the electromobility of the nerve is: 1° unaffected or little affected by the solution, 2° abolished by the solution and restored by soakage in physiological saline, 3° abolished by the solution and not restored in saline.

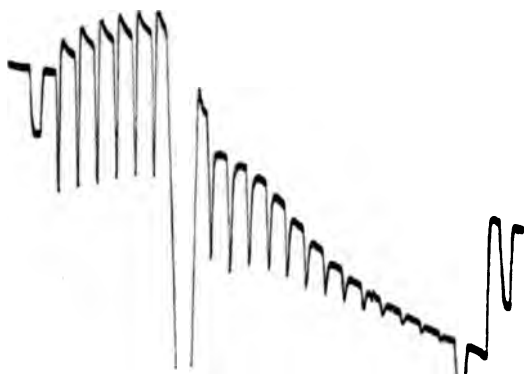
The circumstances of experiment, strength, and duration of excitation, distance between electrodes, are, of course, maintained unvaried. The unavoidable variations of frogs and of their nerves are far less serious than might have been expected; the nerves are removed with



ordinary care, a portion of spinal column being removed with them to serve as handles, and kept until required in physiological saline, which is best made with tap water and must not have the slightest acid reaction. The usual value of the normal response of a satisfactory nerve is between 0.001 and 0.002 volt, and the time during which a nerve may be employed for experiment is usually at the least 24—48 hours after excision. Quite fresh nerves may be used, but it is preferable to use nerves that have remained in physiological saline for an hour or two after the removal from a freshly pithed frog, and it is unadvisable to make use of nerves that have been left for any considerable length of time in the tissues of a pithed frog.

Fig. 3 (Plate 3492) gives the result of a typical experiment upon a frog's nerve submitted to the influence of a strong solution of betaine hydrochloride (10 per cent. neutralised by half its volume of normal soda solution).

FIG. 3 (Betaine hydrochloride).



A summary of our observations is given below; we have included in that summary for the sake of comparison seven observations on a sample of Calmette's snake venom (received from Professor Wright, of Netley), on a sample of tetanus toxine (from Mr. Plimmer, of the Lister Institute), and on some decomposed serum-albumin.

N.B.—Throughout this series of experiments the unit in which the deflection values of the current of injury and the negative variation is expressed = 0.0001 volt.

## Experiment I.—Betaïne Hydrochloride. 2 per cent. solution.

## FIRST NERVE.

|                                            | In 1/10000 of a volt. |                     |
|--------------------------------------------|-----------------------|---------------------|
|                                            | Current of injury.    | Negative variation. |
| After soaking in saline for 2 hours .....  | + 25                  | - 4                 |
| After new transverse section .....         | + off scale           | -15                 |
| After further 12 hours in saline .....     | + 25                  | -19                 |
| After new transverse section .....         | + off scale           | -22                 |
| After soaking in betaïne for 20 mins. .... | + 32                  | -12                 |
| After further 3 hours in betaïne .....     | + 33                  | 0                   |
| After further 9 hours in saline. ....      | + off scale           | -27                 |
| After further 10 hours in saline .....     | + off scale           | -11                 |
| After interpolar crush .....               | —                     | 0                   |

## SECOND NERVE.

|                                             |             |        |
|---------------------------------------------|-------------|--------|
| After soaking in saline for 1 hour .....    | + 18        | - 4    |
| After new transverse section .....          | + off scale | -25    |
| After soaking in betaïne for 1 hour .....   | + 12        | 0      |
| After new transverse section .....          | + 50        | 0      |
| *After soaking in saline for 12 hours ..... | 0           | -2 + 6 |
| *After new transverse section .....         | + off scale | -33    |
| After 1 hour in betaïne .....               | + 50        | 0      |
| After new transverse section .....          | + off scale | 0      |
| After 12 hours in saline .....              | —           | -11    |
| After new transverse section .....          | —           | -17    |

Betaïne, as regards its direct effect upon nerve, is a substance of the second class, as defined above, viz., moderately active. This conclusion is borne out by the similar results of further trials at higher and lower strengths of solution.

## Exp. II.—Betaïne.

## FIRST NERVE.

|          |                                          | Current of injury. | Neg. var. |
|----------|------------------------------------------|--------------------|-----------|
| 0 hours. | In saline for 1 hour .....               | + 25               | - 5       |
| 1        | „ .....                                  | + 22               | - 4       |
|          | New transverse section .....             | + off scale        | - 15      |
| 12       | „ In saline for 12 hours .....           | + 25               | - 19      |
|          | New transverse section .....             | + off              | - 22      |
| 12½      | „ In bet. hyd., 2 p. c. for 25 mins. ... | + 32               | - 12      |
| 16       | „ In bet. hyd. for 3½ hours .....        | + 33               | 0         |
| 25       | „ In saline for 9 hours .....            | + off              | - 27      |
| 35       | „ Ditto for 10 hours .....               | + off              | - 11      |
|          | Then interpolar crush .....              | —                  | 0         |

\* Plate 3503.

## SECOND NERVE.

|          |                                         | Current of injury. | Neg. var. |
|----------|-----------------------------------------|--------------------|-----------|
| 0 hours. | In bet. hyd., 2 p. c., for 1 hour ...   | + 17               | - 4       |
| 1        | " .....                                 | + 12               | 0         |
|          | New transverse section .....            | + 70               | 0         |
| 12       | " In saline for 12 hours* .....         | 0                  | - 1, + 6  |
|          | New transverse section .....            | + off              | - 33      |
| 12½      | " In bet. hyd., 2 p. c., for 1 hour ... | + 54               | 0         |
| 16       | " New transverse section .....          | > +110             | 0         |
| 25       | " In saline for 12 hours.....           | —                  | - 11      |
|          | Then new transverse section .....       | —                  | - 17      |
|          | Then interpolar crush.....              | —                  | 0         |
|          | With reversal of excitation .....       | —                  | 0         |

## Exp. III.—Betaine Hydrochloride. 2 per cent.

Two nerves removed and placed at once in betaine and tested 3½ hours later gave 0 response; transferred to saline and tested 9 hours later, when they gave respectively 0·0025 and 0·0011 volt. After interpolar crush these responses disappeared.

## Exp. IV.—Betaine Hydrochloride. 10 per cent.

|                                           |     |
|-------------------------------------------|-----|
| After 16 hours in saline .....            | - 5 |
| After soaking in betaine for 1 hour ..... | 0   |
| After 4 hours in saline .....             | - 2 |
| Ditto after new transverse section .....  | - 6 |
| After interpolar crush.....               | 0   |

## Exp. V.—Betaine Hydrochloride. 1 per cent.

|                                         |      |
|-----------------------------------------|------|
| After 15 hours in saline .....          | - 5  |
| After 1 hour in betaine .....           | - 10 |
| After 5 hours in betaine .....          | - 1  |
| After 9 hours in betaine .....          | 0    |
| Ditto after new transverse section..... | 0    |
| After further 14 hours in saline.....   | - 3  |
| After further 12 hours in saline.....   | - 4  |
| Ditto after new transverse section..... | - 9  |
| Ditto after interpolar crush .....      | 0    |

## Exp. VI.—Muscarine Hydrochloride. 1 per cent.

|                                                                                 | First nerve. | Second nerve. |
|---------------------------------------------------------------------------------|--------------|---------------|
| Normal response .....                                                           | - 8          | - 14          |
| After soaking in muscarine solution for 5 hours;<br>new transverse section..... | 0            | 0             |
| After soaking in normal saline for 8 hours .....                                | 0            | 0             |

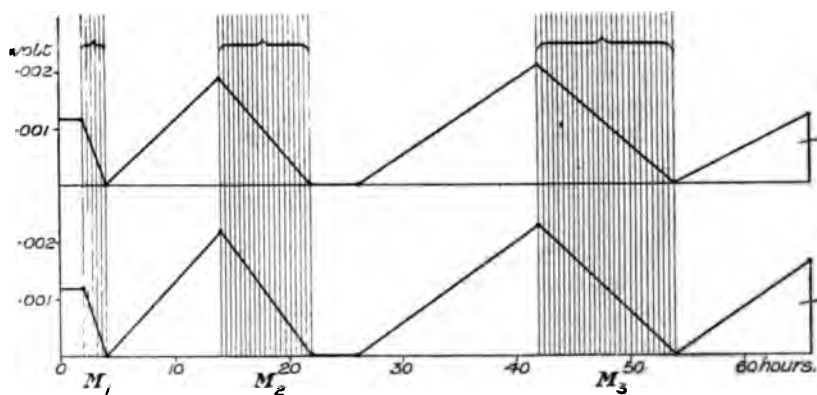
## Exp. VII.—Muscarine Nitrate.

|                                                                     | First nerve. | Second nerve. |
|---------------------------------------------------------------------|--------------|---------------|
| Normal, after 3½ hours in saline and a new transverse section ..... | - 11         | - 18          |
| After 3 hours in muscarine and new transverse section.....          | 0            | 0             |
| After 12 hours in saline and new transverse section.....            | 6            | 6             |

## Exp. VIII (fig. 4).—Muscarine Hydrochloride. 2 per cent. in saline.

|                                                                                    | First nerve.       |           | Second nerve.      |           |
|------------------------------------------------------------------------------------|--------------------|-----------|--------------------|-----------|
|                                                                                    | Current of injury. | Neg. var. | Current of injury. | Neg. var. |
| After soaking in saline for 2 hours and a new transverse section ...               | + 66               | - 12      | off +              | - 12      |
| After soaking in muscarine solution for 2 hours and a new transverse section ..... | + 55               | 0         | + 66               | 0         |
| After 10 hours in saline and new transverse section .....                          | off +              | - 22      | off +              | - 19      |
| After 8 hours in muscarine and new transverse section .....                        | + 80               | 0         | + 60               | 0         |
| After 4 hours in saline .....                                                      | —                  | 0         | —                  | 0         |
| After 16 hours in saline .....                                                     | off +              | - 23      | off +              | - 21      |
| After 12 hours in muscarine.....                                                   | 0                  | 0         | 0                  | 0         |
| After 12 hours in saline .....                                                     | —                  | - 16      | —                  | - 12      |
| After inter-polar crush .....                                                      | —                  | 0         | —                  | 0         |

FIG. 4.



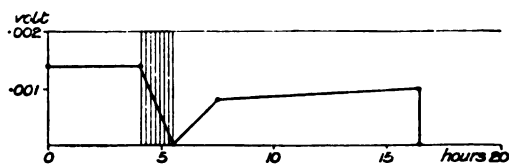
## Exp. IX.—Muscarine; Bétaïne; Choline; Neurine. 1 per cent.

|                                                                                     | Current of injury. | Neg. var. |
|-------------------------------------------------------------------------------------|--------------------|-----------|
| Nerve 1.—Normal .....                                                               | off +              | - 14      |
| After 7 hours in MUSCARINE .....                                                    | off +              | 0         |
| After 3 hours in saline .....                                                       | off +              | 0         |
| After new transverse section .....                                                  | off +              | 0         |
| After further 15 hours in saline .....                                              | off +              | 0         |
| After new transverse section .....                                                  | off +              | 0         |
| Nerve 2.—Normal .....                                                               | + off              | - 10      |
| After 7 hours in BÉTAÏNE .....                                                      | + 8                | 0         |
| After 3 hours in saline .....                                                       | - 3                | - 3       |
| After new transverse section .....                                                  | + off              | - 20      |
| After further 15 hours in saline .....                                              | + 30               | - 10      |
| New transverse section .....                                                        | + off              | - 30      |
| Nerve 3.—Normal .....                                                               | + off              | - 13      |
| After 7 hours in choline .....                                                      | + 17               | - 13      |
| After further 20 hours in CHOLINE .....                                             | + off              | - 4       |
| After new transverse section .....                                                  | + off              | - 7       |
| Nerve 4. — Neurine (neutralised by<br>H <sub>2</sub> SO <sub>4</sub> ). Normal..... | + off              | - 13      |
| After 7 hours NEURINE .....                                                         | + off              | 0         |
| After new transverse section .....                                                  | + off              | - 1       |
| After 18 hours in saline .....                                                      | + off              | - 2       |
| After new transverse section .....                                                  | + off              | - 6       |

## Exp. X (fig. 5).—Stale Cerebro-spinal Fluid (about 4 per cent.).

|                                                             |       |      |
|-------------------------------------------------------------|-------|------|
| After 4 hours in saline and new<br>transverse section ..... | off + | - 14 |
| After 1½ hours in cerebro-spinal<br>fluid .....             | —     | 0    |
| After new transverse section .....                          | —     | 0    |
| After 2 hours in saline .....                               | off + | - 8  |
| After further 9 hours in saline .....                       | + 70  | - 10 |
| After new transverse section .....                          | off + | - 10 |

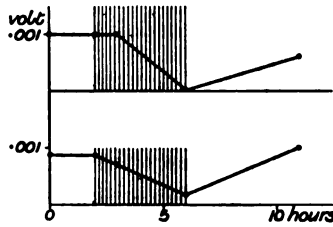
FIG. 5.



Exp. XI (fig. 6).—Snake Venom (Calmette).

|                                                                  | First nerve. | Second nerve. |
|------------------------------------------------------------------|--------------|---------------|
| Normal after 2 hours in saline .....                             | - 9          | - 10          |
| After 1 hour in venom .....                                      | - 7          | - 10          |
| After further 4 hours in venom and a new transverse section..... | - 2          | 0             |
| After 5 hours in saline and new transverse section.....          | - 10         | - 6           |

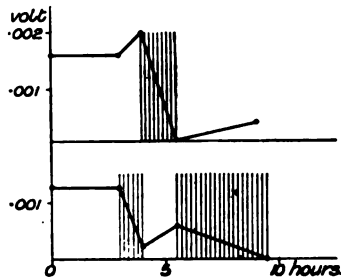
FIG. 6.



Exp. XII (fig. 7).—Snake Venom (Calmette). (Two nerves.)

|                                                                 |      |
|-----------------------------------------------------------------|------|
| Normal after 3 hours in saline and new transverse section ..... | - 16 |
| After 4 hours in saline and new transverse section ...          | - 20 |
| After 1½ hours in venom and new transverse section...           | 0    |
| After 3½ hours in saline .....                                  | - 4  |
| Normal after 3 hours in saline and new transverse section       | - 13 |
| After 1 hour in venom and new transverse section.....           | - 2  |
| After 1½ hours in saline and new transverse section.....        | - 6  |
| After 4 hours in venom and new transverse section.....          | 0    |

FIG. 7.



## Exp. XIII.—Venom + Antivenom.

|                                                                                | (Two nerves.) |      |
|--------------------------------------------------------------------------------|---------------|------|
| Normal after $3\frac{1}{2}$ hours in saline and new transverse section .....   | - 14          | - 14 |
| After 11 hours in venom + antivenom and new transverse section.....            | 0             | 0    |
| After 2 hours in saline and new transverse section.....                        | 0             | 0    |
| After further $12\frac{1}{2}$ hours in saline and new transverse section ..... | - 10          | - 10 |
| After interpolar crush.....                                                    | 0             | 0    |

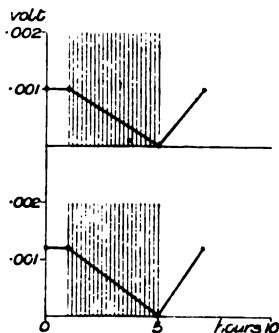
## Exp. XIV.—Venom + Antivenom.

|                                                                    |      |
|--------------------------------------------------------------------|------|
| Normal after 1 hour in saline .....                                | - 10 |
| After 1 hour in venom + antivenom and new transverse section ..... | 0    |
| After 2 hours in saline and new transverse section ...             | - 10 |
| After further 5 hours in saline.....                               | - 5  |
| Then with new transverse section .....                             | - 20 |
| After 1 hour in venom + antivenom .....                            | - 20 |
| After 1 hour further in venom + antivenom .....                    | - 20 |
| After 1 hour further in venom + antivenom .....                    | 0    |

## Exp. XV (fig. 8).—Diphtheritic Toxine.

|                                                                            | (Two nerves.) |      |
|----------------------------------------------------------------------------|---------------|------|
| Normal .....                                                               | - 12          | - 10 |
| After bath of 4 hours and new transverse section .....                     | 0             | 0    |
| After subsequent bath of saline for 2 hours and new transverse section ... | - 12          | - 10 |

FIG. 8.



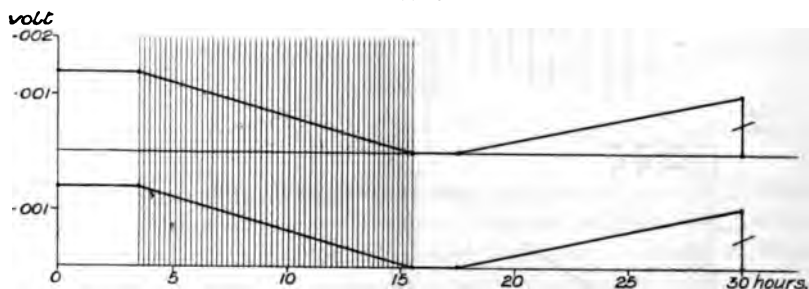
## Exp. XVI.—Tetanus Toxine.

|                                                                 | In tetanine. |       |       | In saline. |       |      |
|-----------------------------------------------------------------|--------------|-------|-------|------------|-------|------|
| Normal responses of six fresh nerves.....                       | - 21,        | - 20, | - 25, | - 16,      | - 26, | - 18 |
| After 1 hour in toxine and new transverse section.....          | - 10,        | - 5,  | - 3,  | —          | —     | —    |
| Ditto control nerves in saline and new transverse section ..... | —            | —     | —     | - 21,      | - 18, | - 21 |
| After 3 hours in toxine and new transverse section .....        | - 2,         | 0,    | 0,    | —          | —     | —    |
| Ditto control nerves in saline and new transverse section ..... | —            | —     | —     | - 20,      | - 18, | - 20 |

## Exp. XVII (fig. 9).—Decomposed Serum-Albumin.

|                                                           | (Two nerves.) |               |
|-----------------------------------------------------------|---------------|---------------|
|                                                           | First nerve.  | Second nerve. |
| Normal after 5 hours in saline .....                      | - 11          | - 10          |
| After 1 hour in albumin and new transverse section.....   | 0             | 0             |
| After 3½ hours in saline .....                            | - 10          | - 10          |
| After 2½ hours in albumin and new transverse section..... | 0             | 0             |
| After 13 hours in saline and new transverse section.....  | - 7           | - 6           |
| After interpolar crush .....                              | 0             | 0             |

FIG. 9.



## Exp. XVIII (figs. 10 and 11).—Decomposed Serum-Albumin.

1. Normal series of negative variations; nerve previously kept for 3 hours in normal saline; coil at 20 units.



2. Abolition of the variation ; same nerve soaked for 1 hour in a putrid solution of serum-albumin.
3. Recovery ; same nerve left for 12 hours in normal saline.
4. Abolition ; same nerve left for  $2\frac{1}{2}$  hours in putrid serum-albumin.
5. Recovery ; same nerve for  $4\frac{1}{2}$  hours in putrid serum-albumin.

FIG. 10.

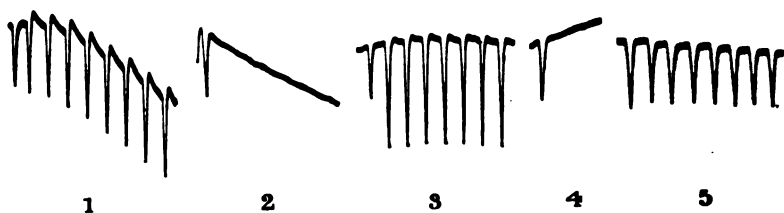
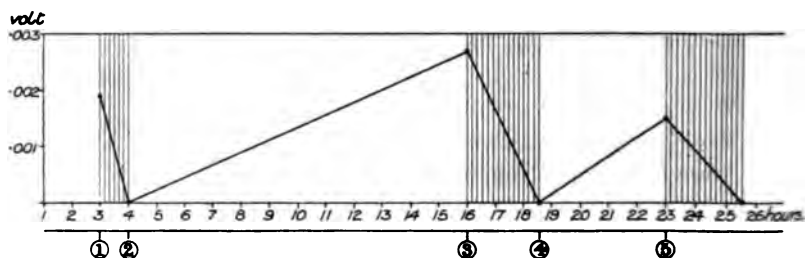


FIG. 11.



*Remarks on the foregoing Experiments (I to XVIII).*

EXP. I. *Betaine Hydrochloride 2 per cent.*—This nerve exhibits abolition by betaine and recovery by saline twice repeated.

The companion nerve exhibited a similar result twice repeated. The plotted curve (fig. 12) gives the magnitude of the negative variation.

FIG. 12.

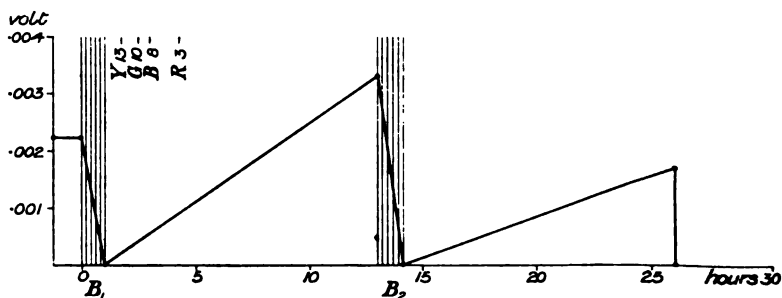


Fig. 13 is given to illustrate the refreshing effect of a new transverse section upon a small negative variation. It is not special to this particular experiment, but illustrative of a general rule of procedure that should be adopted in prolonged experiments.

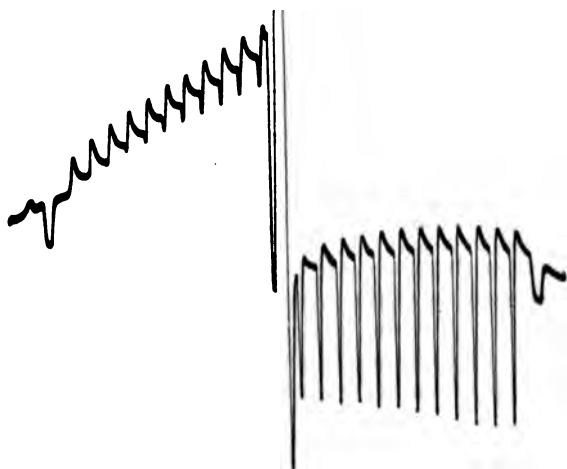
EXP. II. The two nerves of the same frog are similarly but simultaneously passed through the solutions.

From Exps. I to V we think ourselves justified in estimating betaine as belonging to the second of the three classes specified above, *i.e.*, as "moderately active." The electromobility of nerve, as evidenced by the negative variation of its current of injury has been abolished by betaine and restored by subsequent prolonged immersion in physiological saline.

The three following experiments show that muscarine has a similar effect, but rather more pronounced; the negative variation was permanently abolished in Exp. VI (also in Exp. IX).

Exp. VIII, in which two nerves were similarly treated, is the most complete; it exhibits in both cases abolition by muscarine and recovery by saline, three times repeated.

FIG. 13 (Exp. I).



Exp. IX. In order to make comparison as closely as possible between the individual members of the ptomaine group, we took four nerves, as nearly as possible similar, and passed them simultaneously through each of the four test solutions and through physiological saline.

The negative variation of nerve 1, immersed for 7 hours in muscarine, was completely and permanently abolished. That of nerve 2 for 7 hours in betaine was temporarily abolished. That of nerve 3, after 7 hours in choline, was unaffected, and after 27 hours diminished.

That of nerve 4, in neurine for 7 hours, was temporarily abolished and permanently diminished.

Exp. X. The sample of cerebro-spinal fluid used in this experiment was one sent to us 3 weeks previously by Dr. Mott (and that had been tested when fresh with a negative result). On the assumption that the fluid had contained choline (which is comparatively inert), we argued that it should be found to have increased in activity in consequence of oxidation. This was found to be the case; the negative variation of the nerve was temporarily abolished by an immersion lasting  $1\frac{1}{2}$  hours. A similar effect is produced by the action of decomposed serum-albumin, *vide infra* Exps. XVII and XVIII.

Exps. XI to XVI were made with various toxins sent to us by Professor Wright and by Dr. Plimmer. Snake venom (Exps. XI and XII), caused temporary abolition, and we could not, by our method of testing, find any difference of effect when the toxin was mixed with its appropriate quantity of antitoxine solution (Exps. XIII and XIV). Diphtheritic toxin (Exp. XV) and tetanus toxin also produced temporary abolition.

These few experiments, as far as they go, indicate that the toxins in question are, as regards isolated nerve tested in this manner, substances of the second degree of toxicity. But we evidently need further experiments.

The last two experiments (XVII and XVIII) were made to see whether the decomposition products of serum-albumin have a toxic action. It is evident that they have, and that their toxicity is one of the second degree, as defined above.

#### EXPERIMENTS ON THE FROG'S HEART.

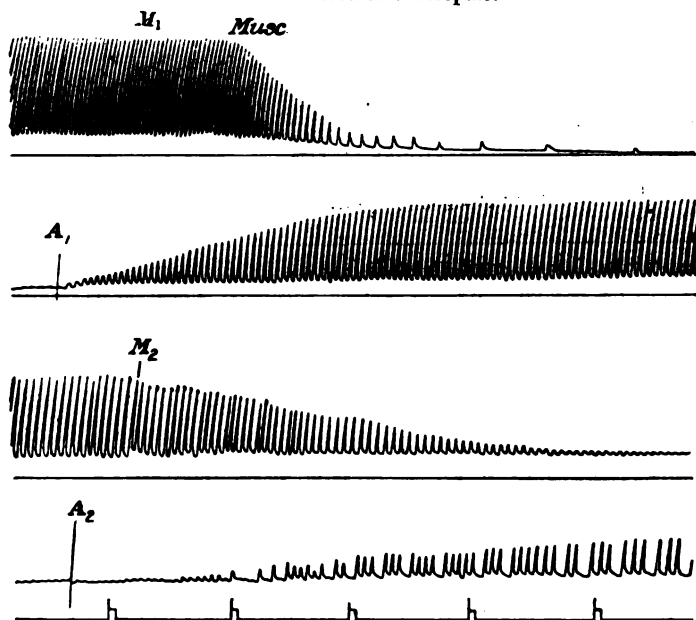
In view of the well-known cardiac effects of muscarine, we undertook an experimental survey of the influence of the group of related bodies upon the action of the heart, taking as the most convenient case for our purpose the isolated frog's heart and the suspension method, the drug, in appropriate dilution being simply applied to the surface of the heart.

The general results of these observations were to the following effect:—

1. Neurine, muscarine, choline, betaine (as hydrochlorides) bring about diastolic arrest of the heart.
2. The arrest thus produced is antagonised by atropine (as sulphate).
3. Neurine and muscarine are more active than betaine or choline.

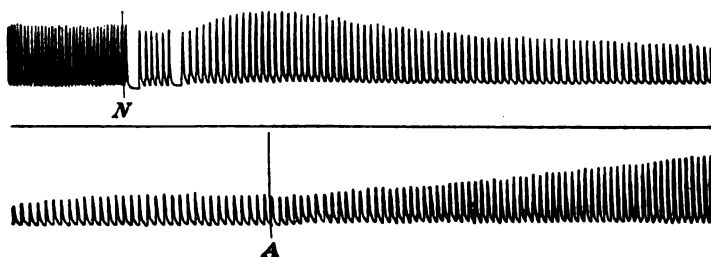
The following records are illustrative examples selected from a series of upwards of 50 experiments, all giving concordant results:—

FIG. 14.—Muscarine-Atropine.



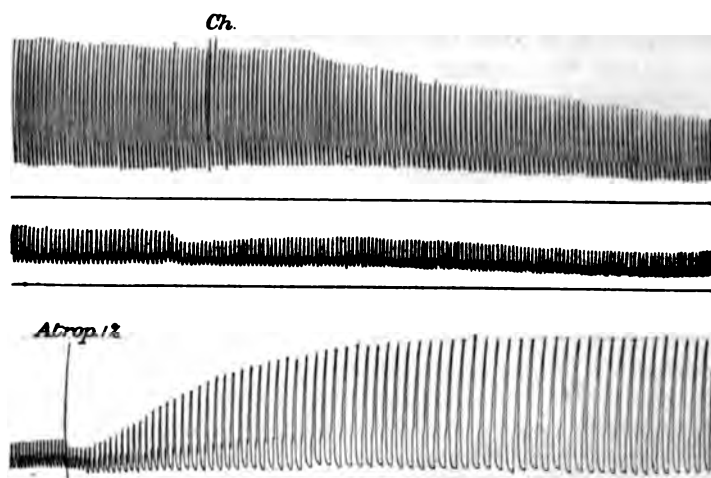
Frog's heart; suspension method. Four successive applications of muscarine hydrochloride (1 per cent. solution in normal saline) and of atropine sulphate (1 per cent.) at the points marked  $M_1$ ,  $A_1$ ,  $M_2$ ,  $A_2$  on the four successive lines. The record exhibits an antagonism of muscarine by atropine and *vice versa*—i.e., contrary to the usual statement, a bilateral antagonism is sometimes demonstrable between these two drugs.

FIG. 15.—Neurine-Atropine.



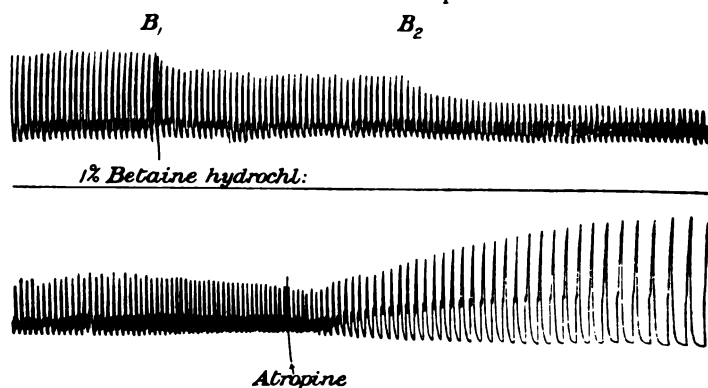
Frog's heart. Effect of neurine applied at the point N. 1 per cent. solution neutralised by  $H_2SO_4$ . Subsequent application of atropine sulphate, 1 per cent. solution, at A.

FIG. 16.—Choline-Atropine.



Frog's heart. Effect of choline hydrochloride at Ch., 2·5 per cent. solution in normal saline. Subsequent application of atropine sulphate, 1 per cent. solution.

FIG. 17.—Betaïne-Atropine.



Frog's heart. Effect of betaïne hydrochloride, 1 per cent. solution neutralised by NaOH, applied at B<sub>1</sub> and B<sub>2</sub>. Subsequent application of atropine sulphate, 1 per cent. solution.

*Conclusion.*—The general conclusion to be drawn for the above experiments on isolated nerve and on the excised heart is that the order of toxicity of the four ptomaines examined is:—

- 1stly. Neurine and muscarine.
- 2ndly. Choline and betaïne.

The first two substances are considerably more toxic than the second two; and for each of the two pairs the first named has shown itself to be somewhat the more toxic.

As regards the excised heart, the effect of all four substances is arrest in diastole; the effect is in each case counteracted by atropine.

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“The Physiological Action of Betaine extracted from Raw Beet-Sugar.” By A. D. WALLER, M.D., F.R.S., and R. H. ADERS PLIMMER, D.Sc. (Grocers’ Research Student, Jenner Institute of Preventive Medicine). Received June 12,—Read June 18, 1903.

(From the Physiological Laboratory of the University of London, and the Chemical and Water Laboratory of the Jenner Institute of Preventive Medicine.)

### PART 1 (A. D. W.).

From the observations described in the preceding communication, it was evident that betaine cannot be distinguished as an inert member of the ptomaine series, at least as regards its action on isolated nerve and on the isolated heart. This led to an inquiry into the original source of the universal text-book statement that betaine, unlike choline, neurine and muscarine, is non-toxic. The only experimental evidence to the point consists (as far as I have yet discovered\*) in a statement by Schultzen, quoted by Scheibler in the ‘*Berichte der Deutschen Chemischen Gesellschaft*’ for 1870, vol. 3, p. 155, to the following effect:—

“Mehrere Versuche welche ich mit dem Betaïn ausstellte, haben übereinstimmend ergeben dass dasselbe in keiner Weise giftig wirkt, ja keinerlei wahrnehmbare Wirkungen auf das Befinden eines Thieres

\* K. Andrlík, A. Velich, and Vl. Staněk, in a quite recent paper (“Das Betaïn in Physiologisch-chemischer Beziehung. Vorläufige Mittheilung,” ‘*Cbt. für Physiologie*,’ November 22, 1902, p. 452), confirm Scheibler’s statement, saying:

“Es ergab sich [an Froschen, weissen Ratten und Hunden] dass die direkte injection dieses Stoffes [Betaïn] in das Blut selbst in grösseren Mengen [keine erkennbaren Aenderungen der physiologischen Functionen herbeiführt. Direkte Messungen des Blutdruckes bei curaresirten Hunden haben gezeigt, dass [das Betaïn den Blutdruck absolut nicht beeinflusst. Es war nur eine unbedeutende Pulsretardation zu vermerken. Andere sichtbare Symptome konnten nicht constatirt werden.”

They injected 5 grammes *per venam* into a dog and recovered nearly the whole of this amount from the urine in an unaltered state. *Per os* only about one-third of the betaine administered was recovered from the urine. From a cow having taken 144 grammes *per os* none was recovered.

hat, selbst wenn es in grossen Dosen, z. B., 1 Gramm auf einmal direkt ins Blut (eines Kaninchens) gebracht wird."

The experiments to be described below are in direct contradiction of this very clear and positive statement.

In a series of experiments made with a different object in view, viz., to determine the effect upon isolated nerve of different kinds of sugar, it was noticed more than once that syrups made with ordinary beet-sugar had a faint cadaveric odour reminiscent of the choline and neurine solutions that had just been under investigation, and the suspicion was naturally aroused that the taint of the samples in question might be due to the presence of betaine or of allied alkaloid. I attempted (and failed) to separate betaine from such a sample; Dr. Plimmer has undertaken the task again with a positive result.

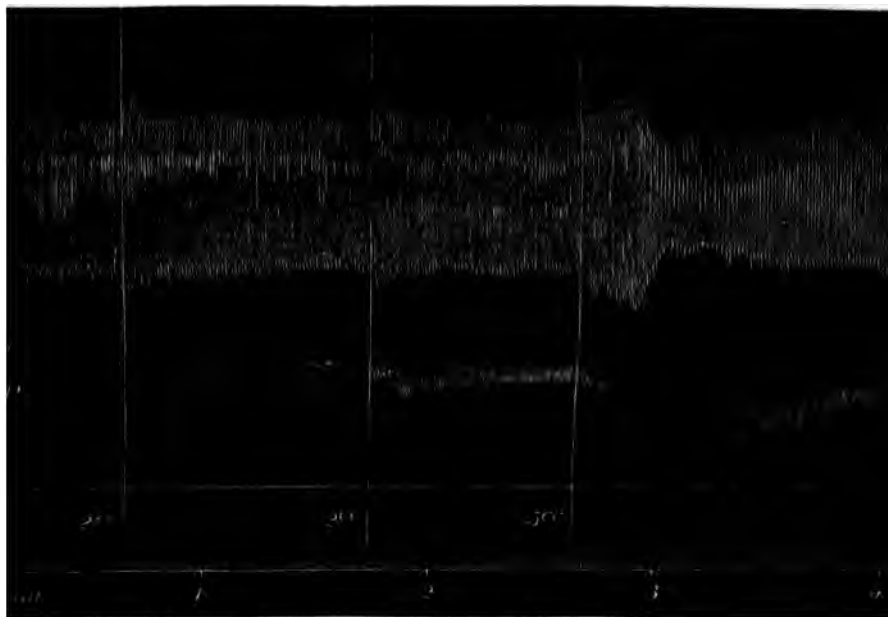
*Physiological Data.*—The action of betaine (as hydrochloride) upon isolated nerve and the isolated heart has been described in the previous paper. All that remained to do in the present connection was to re-try upon warm-blooded animals the effects upon respiration and upon blood pressure the effects of intravenous injections of betaine.

### Experiments.

| Date.      | Animal.    |             |                   | Per kilo. | Effect.                                                              |
|------------|------------|-------------|-------------------|-----------|----------------------------------------------------------------------|
| Mar. 12... | Dog ....   | kilos. 15.0 | gramme. 1.0 B     | 0.067     | No marked effect; subsequently death by muscarine injection.         |
| June 3...  | Cat .....  | 4.4         | 0.5 B             | 0.114     | Sudden death by cardiac inhibition.                                  |
| " 4...     | Rabbit ... | 2.0         | 0.1 + 0.1 + 0.1 B | 0.150     | Dyspnoic convulsions; cardiac arrest followed by a few respirations. |
| " 4...     | Cat .....  | 1.0         | 0.1 B             | 0.100     | Ditto ditto                                                          |
| " 6...     | Cat .....  | 3.2         | 0.5 B'            | —         | The 2nd dose was fatal.                                              |
| " 6...     | Cat .....  | 2.7         | 0.2, 0.2, 0.5 B'  | —         | The 5th dose was fatal.                                              |
| " 7...     | Cat .....  | 3.1         | 0.2, 0.2, 0.4 B'  | —         | The 4th dose was fatal.                                              |
|            |            |             | 0.3 B             |           |                                                                      |

B = Commercial betaine (Merck).

B' = Betaine from sugar (Plimmer).



No. 6.—Cat, 2.6 kilos. Respiration and blood-pressure record. Three successive injections of betaine hydrochloride, 10 per cent. solution, neutralised by NaOH (extracted from raw beet-sugar by Dr. Plimmer). (See continuation on following page.)

It appears from these experiments that betaine (as hydrochloride injected *per venam*) acts directly upon the heart; that commercial betaine (Merck) is more powerful than betaine extracted from beet-sugar (Plimmer).

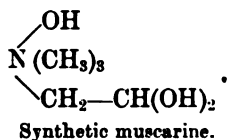
In all instances the mode of death has been by cardiac syncope from which no recovery could be obtained by artificial respiration. With sublethal doses the characteristic effect was a temporary fall of blood pressure, with a slight augmentation of the respiratory movements.

The difference of action between commercial betaine and betaine from sugar gave rise to several reflections. Unlike muscarine, of which at least two chemical varieties are known, having quite different physiological actions, betaine is a single well-defined chemical substance that, if pure, should be of constant composition and action. Analysis of a commercial sample of betaine (Schuchardt) by Dr. Plimmer revealed the rather surprising fact that the sample in question contained a large proportion of potassium chloride, quite enough to exercise a direct depressant effect upon the heart's action. The difference between commercial and laboratory betaine is thus very probably due to impurity in the former.





although the muscarine synthetically prepared by the oxidation of choline has a slightly different constitution, namely,\*



The presence of betaine in raw beet-sugar, in which small quantities might reasonably be suspected, has, so far as I have been able to ascertain, not yet been demonstrated, and the object of this investigation has been to determine whether it is present, and if so, in what quantity.

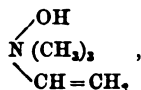
On account of the presence of perhaps only a very small amount of betaine in raw beet-sugar (the juice of the ripe beet containing only  $\frac{1}{10}$  per cent., that of the unripe  $\frac{1}{4}$  per cent.), two preliminary experiments were made to see if it were possible to extract  $\frac{1}{10}$  per cent. of it from sugar to which it had been added; in the first of these, the sugar was removed as insoluble lead saccharate according to the method patented by Wohl,<sup>4</sup> and in the other it was not removed. In both cases phosphotungstic acid, as used and recommended by Scheibler, was used to precipitate the betaine.

1. 100 grammes of sugar, to which 0.1 gramme of betaine hydrochloride was added, were dissolved in 250 cc. of water, and to this solution, warmed on the water-bath, 150 grammes of lead oxide were gradually added; the mixture being meanwhile well stirred. The insoluble lead saccharate so formed was then filtered off, and well washed, and the filtrate, treated with sulphuretted hydrogen to remove traces of lead which had gone into solution, was evaporated down to a small volume; 1 gm. of phosphotungstic acid in 10 cc. of water, acidified with sulphuric acid, was then added to it, and on standing, white crystals were gradually precipitated; after a month these were filtered off, washed with water, and when dried at 100° C. weighed 0.8 gramme. On decomposition 0.1 gramme of betaine hydrochloride, melting at 237° C., was obtained. The original substance melted at 237°—238° C.

Betaine can thus be quantitatively recovered from sugar to which it has been added.

2. The same quantity of sugar and of betaine hydrochloride were dissolved in 100 cc. of water, and the same quantity of phosphotungstic

\* The term neurine now designates the compound with the following formula:—



which is seen to contain 1 molecule of water less than choline.

acid added; after the same time, however, only a very small quantity of white crystals were precipitated, but on adding a large excess of phosphotungstic acid, and allowing the solution to stand another week, white crystals were gradually precipitated, which, when washed and dried at 100° C., weighed 0.6 gramme.

These observations show that the presence of sugar slightly hinders the precipitation of betaine by means of phosphotungstic acid, and that in order to precipitate it under these conditions a large excess of the reagent is required.

When working with large quantities of sugar, this method of removing sugar with lead oxide is almost impossible to carry out in the laboratory. I was led, therefore, to adopt a different method, utilising the ready solubility of betaine in alcohol; a certain quantity of sugar is also dissolved, but this is insufficient to prevent the precipitation of betaine by phosphotungstic acid, and as the above experiment shows, it can be practically completely precipitated by excess of the reagent.

1000 grammes of raw beet-sugar were exhaustively extracted in two portions of 500 grammes each, with 2 litres of methylated spirit. The alcoholic extract so obtained was evaporated down *in vacuo* to a syrup, the syrup dissolved in  $\frac{1}{2}$ — $\frac{3}{4}$  litre of water, and to this solution, warmed on the water-bath, 200 c.c. of phosphotungstic acid solution (30 per cent. + 5 per cent.  $\text{H}_2\text{SO}_4$ ) were added. A brownish crystalline precipitate was obtained, which was filtered off after it had stood for a week, so as to complete the precipitation, washed with a little water, and dried at 100° C; it weighed 50 grammes. This precipitate, suspended in water, was then decomposed with excess of baryta, and the filtrate from the insoluble barium phosphotungstate was evaporated down to dryness, after removal from it of excess of baryta by means of carbon dioxide; the brown residue so obtained was dissolved in alcohol, acidified with hydrochloric acid, and treated with 10 grammes of mercuric chloride dissolved in alcohol; betaine hydrochloride in combination with mercuric chloride was thus precipitated in white crystalline needles free from the brown colouring matter; on decomposing it in aqueous solution with sulphuretted hydrogen, and evaporating to dryness, white crystals of betaine hydrochloride were obtained, weighing 2.3 grammes; recrystallised once from alcohol they were obtained quite pure, and melted at 238°—239° C. with decomposition. (The melting point of betaine hydrochloride obtained by Jahns<sup>3</sup> from wormseeds, *Artemisia cina*, melted at 227°—228° C., but this is in all probability too low. A specimen obtained from Merck melted at 237°—238° C. A synthetical specimen from Schuchardt, after separation from it of about 80 per cent. of potassium chloride, melted at 237°—238° C.)

Analyses of the substance obtained from raw beet-sugar and dried at 100° C. gave the following result:—

- (1.) 0.2150 gramme substance, by Kjeldahl's method, gave 0.00198 gramme N.  
 (2.) 0.2075 gramme substance gave 0.1930 gramme AgCl.

| Calc. for $C_5H_{11}NO_2Cl$ . | Found. |       |
|-------------------------------|--------|-------|
|                               | I.     | II.   |
| N = 9.13 per cent.            | 9.21   | —     |
| Cl = 23.08 „                  | —      | 22.96 |

The alcoholic filtrate from the compound of betaine hydrochloride with mercuric chloride was evaporated down, the residue dissolved in water, and decomposed with sulphuretted hydrogen; the solution filtered from mercuric sulphide, evaporated to dryness, yielded a further 2.1 grammes of betaine hydrochloride, coloured brown; by treatment with cold alcohol most of the colouring matter was removed, and the residue after recrystallisation from alcohol, to which a little animal charcoal was added, was obtained pure and melted at  $237^{\circ}$ — $238^{\circ}$  C. with decomposition. For further characterisation, a portion of it was converted into its compound with gold chloride.

E. Fischer<sup>6</sup> has recently pointed out that betaine gold chloride, when crystallised from water, melts at about  $209^{\circ}$  C., and gives, on determination of the gold, values too low to agree with the formula  $C_5H_{12}O_2NAuCl_4$ ; it is only when crystallised from dilute hydrochloric acid that it gives values agreeing with that formula; he has shown that this compound melts at  $245^{\circ}$  C. (corr.  $250^{\circ}$  C.) when quickly heated, but that the melting point often lies  $10^{\circ}$  lower owing to decomposition if the substance is not quickly heated.

The gold chloride compound obtained, when recrystallised from water, melted at about  $209^{\circ}$ — $210^{\circ}$  C., and gave the following results on analysis:—

- (1.) 0.2502 gramme substance, dried at  $100^{\circ}$  C., gave 0.0998 gramme Au.  
 (2.) 0.2279 gramme substance, dried at  $100^{\circ}$  C., gave 0.0910 gramme Au.

Found (1) Au = 39.89 per cent. ; (2) Au = 39.93 per cent.

A portion recrystallised from dilute hydrochloric acid crystallised in leaflets, melted at  $235^{\circ}$ — $238^{\circ}$  C. with decomposition, and gave the following result on analysis:—

0.2880 gramme substance, dried *in vacuo* over sulphuric acid, gave 0.1264 gramme Au.

Found Au = 43.89 per cent.

$C_5H_{12}O_2NAuCl_4$  requires Au = 43.14 per cent.

This figure, however, is somewhat high; it may be accounted for by the fact that a minute quantity of metallic gold was deposited during recrystallisation.

No more betaine was precipitated on adding 200 c.c. of phosphotungstic acid to the filtrate from the betaine phosphotungstate, the yield of betaine hydrochloride thus being 4.4 grammes from 1 kilo. of sugar.

10 kilogrammes of raw beet-sugar have also been extracted and precipitated with phosphotungstic acid in the same way, and the product obtained was handed to Dr. Waller for physiological investigation.

In order to determine the quantity of betaine in raw beet-sugar more accurately, 100 grammes of the sugar were treated as above described with lead oxide and precipitated with phosphotungstic acid; 6.3 grammes were thus obtained, and these gave on decomposition 0.5 gramme of betaine hydrochloride melting at 236°—238° C.

*Conclusion.*—Betaine in considerable quantity (3.75 per 1000 in the sample examined) is present in raw beet-sugar.

*Note.*—It is perhaps advisable to clearly specify what samples of betaine have actually passed through our hands:—

No. 1 (from Merck's) has been used in the experiments of the previous paper (Waller and Sowton) and in Experiment 6 of the present paper.

No. 2, prepared by one of us (R. H. A. P.) from "raw beet-sugar," was used in the experiments of the present paper.

No. 3 (from Schuchardt), containing potassium chloride, has not been used for any physiological tests.

#### REFERENCES.

- <sup>1</sup> C. Scheibler, 'Zeit. f. Rübenzuckerindustrie,' vol. 16, p. 229; 'Ber. d. Deutsch. Chem. Ges.,' 1869, vol. 2, p. 292; 1870, vol. 3, p. 155.
  - <sup>2</sup> O. Liebreich, 'Ber. d. Deutsch. Chem. Ges.,' 1869, vol. 2, pp. 12, 167; 1870, vol. 3, p. 161.
  - <sup>3</sup> E. O. v. Lippmann, 'Ber. d. Deutsch. Chem. Ges.,' 1887, vol. 20, p. 3201.
  - <sup>4</sup> A. Wohl, 'Ber. d. Deutsch. Chem. Ges.,' 1896, vol. 29, Ref. 375; 'Chem. Centr.,' 1897, II, p. 926.
  - <sup>5</sup> E. Jahns, 'Ber. d. Deutsch. Chem. Ges.,' 1893, vol. 26, p. 1493.
  - <sup>6</sup> E. Fischer, 'Ber. d. Deutsch. Chem. Ges.,' 1902, vol. 35, p. 1593.
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"Note on the Disintegration of Rabid Brain Substance." By J. O. WAKELIN BARRATT, Research Student, Jenner Institute of Preventive Medicine. Communicated by LORD LISTER, O.M., F.R.S. Received July 10, 1903.

(From the Bacteriological Department of the Institute.)

Although no organism causally related to rabies has been demonstrated in the tissues of animals dying of this infection, nevertheless it has long been inferred that the virus consists of an organism, since it is capable of indefinite increase when passed from animal to animal.

It is obvious that, if the virus of rabies is an organism, disintegration of the material in which it is contained will, if sufficiently minute, lead to its destruction.

In order to test this conclusion, the brain of a rabbit which had died of rabies was broken up in a disintegrator\* for 11 hours with sand, cooling being effected by a stream of liquid carbon dioxide in the outer jacket of the apparatus. The disintegrated material inoculated upon two rabbits communicated rabies in each instance.

More thorough disintegration was next attempted. The later form of disintegrator employed by MacFadyen and Rowland in their recent work on micro-organisms was made use of, and the process carried out at the temperature of liquid air. In this apparatus sand is dispensed with, the brittleness of the material ground at this temperature rendering its use unnecessary.

Portions of the brains of rabbits dying of rabies, following upon inoculation with "virus fixe," were thus disintegrated and the product so obtained, mixed with nine parts of normal saline solution, was used for sub-dural injection. Proceeding in this way it was found that disintegration for five minutes failed to abolish the virulence of the material, that disintegration for half to one hour was usually sufficient to abolish it (10 out of 13 experiments), while disintegration for longer periods (up to three hours) always led to its complete abolition.

This result suggested a mechanical destruction of the virus of rabies during disintegration. Before this conclusion could be adopted, however, it was necessary to ascertain whether any substance was produced or set free during disintegration, which was in itself capable of destroying "virus fixe," since it is known that immunising substances are formed by animals infected with, or immunised against, rabies.†

\* 'Journ. of. Physiol.,' 1901-2, vol. 27, p. 53.

† Cp. R. Kraus u. R. Maresch, "Ueber die Bildung von Immunsustanzen gegen das Lyssavirus bei natürlich empfänglichen und unempfindlichen Thieren," 'Zeitschr. f. Hygiene u. Infectiouskrankheiten,' 1902, vol. 31, pp. 528-533.

Accordingly an emulsion, made by adding disintegrated rabid brain substance to 10 parts of physiological salt solution, was intimately mixed with a virulent brain pulp in the proportion of five parts of the former to one of the latter, and the mixture allowed to stand at the room temperature for 24 hours, it having previously been ascertained that a 1-in-60 emulsion of "virus fixe" in physiological salt solution retains its virulence for this period of time. Intra-cerebral injection of the mixture of disintegrated and virulent brain substance, practised upon rabbits, was followed by rabies, thus showing the absence of a rabicide substance in disintegrated rabid brain.

It might seem not improbable that the virus would be destroyed by so low a temperature as that of liquid air. But it has been ascertained by Dr. A. MacFadyen that exposure of rabid brain substance to the temperature of liquid air for three months fails to deprive it of its virulence.

From the above facts it seems difficult to arrive at any other conclusion than that the infective agent in rabies is deprived of virulence by mere mechanical violence, a result which could only be explained on the hypothesis that the virus is of the nature of a living organism.

Brain substance disintegrated by the method above referred to, and mixed with physiological salt solution in the proportion of 1 in 10, when injected intra-cerebrally into a rabbit in doses of 0.1 c.c. and upwards, often causes convulsions terminating in recovery or death according to the dose. An equal amount of a 1-in-10 brain pulp, made by trituration in a mortar, similarly injected, is usually without effect. Convulsions are producible whether the cerebral substance used is healthy or rabid, fresh or kept for some time previously in glycerine. Hence these convulsive phenomena, whatever be their explanation, have no bearing on the nature of rabies.

As regards the main issue raised in this research, the experiments appear to furnish strong confirmation of the view that the virus of rabies is organised in its nature.'

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"On the Effect of Temperature on Carbon-Dioxide Assimilation."

By GABRIELLE L. C. MATTHAEI. Communicated by F. DARWIN,  
F.R.S. Received July 29, 1903.

(Abstract.)

1. The  $\text{CO}_2$ -assimilation of single cherry-laurel leaves has been determined through a range of temperature from  $-6^\circ$  to  $45^\circ \text{C}$ . The amount of  $\text{CO}_2$  assimilated has been arrived at by the difference between the  $\text{CO}_2$ -content of a current of air before and after passing through the illuminated glass chamber containing the leaf.

At each temperature illumination of several different intensities has been employed in order to make certain that the amount of assimilation is not being limited by insufficient light. This has been neglected by previous investigators, and quite erroneous results have been put forward.

Taking this precaution, there is obtained for each temperature a *maximal assimilation specific to that temperature*. The amount of light required to produce the specific maximal assimilation varies directly with the magnitude of the maximum. When this is once reached, further increase in the illumination or in the amount of  $\text{CO}_2$  supplied produces no longer any augmentation of the assimilation.

2. When a leaf is exposed to light of high intensity the absorbed excess of radiation raises the temperature of the leaf above that indicated by an adjacent thermometer. Under the conditions holding in these experiments, this excess sometimes amounted to as much as  $10^\circ \text{C}$ . It became, therefore, absolutely essential to know the effective internal temperature of the leaf. This has been determined by inserting a very fine thermo-electric junction into the substance of the leaf, and determining the temperature by means of a galvanometer at intervals throughout the assimilation experiment.

3. Care was taken that the leaves employed in these experiments should be all initially in the same condition, since ancillary researches had shown that differences in previous nutrition and temperature may be disturbing factors in the results obtained. The leaves to be employed were cut some time previously and kept, as a preliminary, under similar conditions of illumination and temperature.

In the course of the experiments it came out clearly that there are marked seasonal variations in the absolute assimilatory power of cherry-laurel leaves from the same individual plant.

4. For determining the "real assimilation" under any conditions a valuation of the concurrent respiratory  $\text{CO}_2$ -production is essential. At low temperatures the respiration is small in proportion to the assimilation, and slight errors in valuation are not significant. The



respiratory allowance could then be arrived at by determining the  $\text{CO}_2$ -production of a number of similar leaves in the dark.

At moderately high temperatures the respiration of the actual single leaf employed was determined, where possible, both before the assimilation experiment and after, when the  $\text{CO}_2$ -production is always much increased.

At the highest temperatures rapid decline of vitality made this procedure impossible, and only an approximate value could be arrived at.

5. Taking all these factors into consideration, a satisfactory series of assimilation maxima for the whole range of temperature was finally obtained.

The amount is just determinable at  $-6^\circ \text{C.}$ , and then rises rapidly with higher temperatures, giving a curve which is convex to the temperature abscissa. The curve is similar to the accepted curves for the effect of temperature on respiration, and it rises more and more steeply at higher temperatures—certainly up to  $38^\circ \text{C.}$

At temperatures about this point the leaf is not capable of maintaining its initial high rate of assimilation for any long time, so that the values obtained for successive hourly estimations with the same leaf form a rapidly declining series. The higher the temperature the shorter the duration of the period of maximal assimilation, and it becomes experimentally impossible with hourly estimations to obtain the maximal value at temperatures close to the fatal temperature of  $45^\circ \text{C.}$  The final numbers actually obtained, which can be only *sub*-maximal, show a conventional "optimum" at a temperature about  $38^\circ \text{C.}$ , with a subsequent very rapid decline.

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"An Experimental Investigation of the *Rôle* of the Blood Fluids in connection with Phagocytosis." By A. E. WRIGHT, M.D., late Professor of Pathology, Army Medical School, Netley, Pathologist to St. Mary's Hospital, W., and STEWART R. DOUGLAS, M.R.C.S., Captain, Indian Medical Service. Communicated by Sir JOHN BURDON SANDERSON, Bart., F.R.S. Received September 1, 1903.

It is still a matter of uncertainty whether the blood fluids perform any rôle in connection with phagocytosis.

Certain facts suggest that the rôle of the blood fluids, if it comes into consideration at all, is very subordinate. The facts we have in view are, on the one hand, the facts brought forward by Metchnikoff to show that bacteria may be ingested in the living condition, and on the other hand those, brought forward by one of us in conjunction with Captain F. Windsor, I.M.S.,\* which show that the human serum exerts absolutely no bactericidal action on the staphylococcus pyogenes, the micrococcus melitensis and the plague bacillus.

These facts are, however, not conclusive. They are not inconsistent with the idea that the blood fluids, apart from actually killing the particular pathogenic bacteria here in question, may in some way co-operate in their destruction.

What are required for the resolution of the problem are experiments in which the phagocytes are tested apart from the blood fluids.

The experimental methods which we now pass on to describe enable these crucial experiments to be made.

#### *Methods of Experimentation.*

We have employed a modification of the method of measuring the phagocytic power of the blood, which was devised by Major W. B. Leishman, R.A.M.C.†

In the procedure described by this author equal volumes of a bacterial suspension of appropriate density and of blood drawn from the finger are measured off in a capillary tube, mixed on a slide and covered in with a cover-glass. The blood and bacterial culture are then left in contact for 15 minutes in an incubator standing at blood heat. After this interval the cover-glass is, if necessary, loosened from the slide by a drop of physiological salt solution, and the slide and cover-glass are drawn apart by a sliding movement.

\* Wright and Windsor, 'Journal of Hygiene,' vol. 2, No. 4, Oct., 1902.

† 'Brit. Med. Journ.,' Jan. 11, 1902.

The films thus obtained are stained by Leishman's\* modification of Romanovski's stain, and are subjected to examination under an immersion lens. By enumerating the bacteria ingested in a number of polynuclear white blood corpuscles and dividing, an average is obtained. This average is taken as the measure of the phagocytic power of the blood. It is compared, when comparative experiments are made, with the phagocytic power of a normal blood.

We have modified this method for our purposes (a) by conducting the phagocytosis in capillary tubes, making afterwards film preparations in the ordinary way; (b) by decalcifying the blood with citrate of soda, thus avoiding the complications introduced by blood coagulation, and making it possible to separate the white corpuscles from the blood fluids by centrifugalisation, decantation and washing.

Three different procedures, varying only in details, were employed in our experiments.

*Procedure No. 1, Employed where Nothing more than a Comparison between Bloods from Different Sources or Bloods Subjected to Different Conditions is Required.*

Having provided ourselves with a simple capillary pipette, furnished with a rubber teat and a pencil mark on the stem, we aspirate into the stem of the pipette—dividing off by bubbles of air in accordance with the procedure introduced by one of us—one volume of blood from the finger, one volume of a 1-per-cent. solution of citrate of soda in physiological salt solution, and one volume of a bacterial† suspension made by shaking up a 24-hour agar culture in physiological salt solution and centrifugalising so as to remove any bacterial clumps. We mix together the three equal volumes of blood, bacterial suspension and citrate of soda solution, by blowing these out upon a clean slide and re-aspirating several times in succession. Mixture completed, an aliquot portion of the mixed fluids, such as suffices for our purposes, is drawn up into the capillary stem, and the orifice of the capillary tube is sealed in the flame. This done, the pipette is placed either in an incubator standing at 37° C. or in a vessel of water kept at this temperature.

After the lapse of 15 minutes we break off the extremity of the pipette, carefully mix the contents so as to get an average sample. and proceed to make films, and then to stain them by Leishman's dye.

\* 'Brit. Med. Journ.,' 1901.

† This bacterial suspension may conveniently contain about 10,000,000,000 bacteria in the cubic centimetre. The number may be readily adjusted by the help of the method of enumeration under the microscope described by one of us in the 'Lancet,' July 5, 1902.

*Procedure No. 2, Employed where we Desire to Elicit Separately the Rôle of the White Corpuscles and the Blood Fluids in Phagocytosis, and to Study the Effect Produced by Experimental Modifications of one or other of these Elements Separately.*

Having provided ourselves with a capsule with a recurved limb (such a capsule has already been figured in a previous communication),\* we introduce into it such a quantity of mercury as will fill it to about one-third of its capacity. Having marked off by a pencil mark (made with a glass writing pencil) the level at which the upper surface of the mercury stands, we displace the mercury in such a manner as to cause it to occupy the middle instead of the lower region of the capsule. We again mark off on the outside of the capsule the upper limit of the mercury.

Then, emptying out this last, we bend round in the flame the curved limb in such a manner as to cause it to lie in the plane of the equator of the capsule. This enables us to siphon into it from a watch glass, filled and placed ready to hand, the citrate of soda solution. We introduce of this solution such a quantity as suffices to fill the capsule up to the level of the first pencil mark. This done, we draw blood from the finger and let it run into the capsule until the combined volume of citrate of soda solution and blood attains the level of the second pencil mark.

Having sealed up the upper orifice in the flame—rarefying as we do so the air in the interior of the capsule by the application of warmth—we shake up the contents and suspend the capsule by means of its curved limb into the receptacle of the hand centrifugal machine.

When centrifugalisation has caused the corpuscles to settle to the bottom, we pipette off and reserve the supernatant citrated plasma and replace it by physiological salt solution. In conducting this last operation we employ a capillary pipette, and we carry down its orifice to the very bottom of the capsule in such a manner as effectively to mix up the corpuscles and the newly added fluid. We wash and centrifugalise in this manner three times. The upper layers of the corpuscular deposit, containing as they do a large proportion of white corpuscles, supply the phagocytes required for experimentation.

In the experiments set forth below we mixed in each case three volumes of the upper layers of the washed corpuscular deposit, with three volumes of blood fluid, and one volume of a staphylococcus suspension, containing generally from 7000—10,000 million staphylococci per c.c. The mixture of corpuscles, blood fluid and staphylococci was kept in each case for 15 minutes at a temperature of 37° C., in order to give opportunity for the occurrence of phagocytosis.

\* Wright, 'Roy. Soc. Proc.', vol. 71, 1902.

*Procedure No. 3, Employed where we desire to obtain Citrated Serum for comparison with the Citrated Plasma furnished by Procedure No. 2.*

Where we desire to obtain citrated serum for comparison with the citrated plasma furnished by Procedure No. 2, we graduate our blood capsule in precisely the same manner. Having filled in with blood from the finger up to the first mark, we allow it to clot, and we then introduce into the capsule from a capillary pipette a sufficiency of citrate of soda solution to complete up to the second mark. Finally, we churn up the citrate of soda solution with the blood clot and then centrifugalise.

*Accuracy of the Method and Special Points which come up for consideration in connection with it.*

The accuracy of the method is attested by the concordant results set forth below of the large number of experiments which we conducted in duplicate. We desire to point out that the results incorporated below represent not exceptional fortunate achievements, but simply what may be obtained by the ordinary every-day application of the method.

Before dismissing the consideration of the experimental method, it may be well to elucidate very briefly three points which suggest themselves for consideration in connection with it.

The first of these relates to the calibre of the capillary tubes.

In our earlier experiments we considered it advisable, with a view to providing against a possible cause of fallacy, to conduct our experiments in capillary tubes of a standard calibre. The tubes were in each case calibrated by the method described by one of us,\* to wit, by introducing into the wide end of a tube drawn out in the flame 5 c.mm. of mercury from an "automatic pipette," and marking off that portion of the capillary stem where this quantum of mercury formed a column 5 cm. in length. The experiments which we conducted with calibrated tubes are those which occupy the two next following sections of this paper.

In our later experiments, to wit, in the experiments which occupy the later sections of this paper, we discarded calibrated for uncalibrated tubes, making only the condition that the capillary tubes employed in comparative experiments should appear to the eye to be more or less comparable in calibre. It will be seen, on looking into our results, that the concordance obtained was not less in the case where uncalibrated tubes were employed than in the case where calibrated tubes were employed.

\* 'Transactions of the Roy. Medico-Chirurg. Soc.,' vol. 86, and 'Lancet,' July 5, and Dec., 1902.

Different results, however, emerge when experiments in duplicate are conducted with tubes presenting extreme differences in calibre. In a series of comparative experiments, in which we employed in each case an almost hair-fine capillary tube as a fellow to a tube almost too large to be reckoned as a capillary tube, the results were irregular, being generally but not consistently in favour of the narrower tube.

A *second point* which comes up for consideration is the possible effect of the addition of citrate of soda to the blood.

The concentration of the solution in particular comes into consideration. Finding that phagocytosis is inhibited when the white corpuscles are bathed in a medium containing 3 per cent. of citrate of soda, we took the precaution to add to the blood in comparative experiments precisely the same amounts of citrate of soda. It may be noted that the morphological structure of the white corpuscles is extremely well preserved, and phagocytosis proceeds actively in a medium containing up to 1.5 per cent. of citrate of soda.

The *third* and last *point* to be considered relates to the maintenance of the activity of the phagocytes for a sufficient period after they have been withdrawn from the organism and have been subjected to the procedures described above. It will be manifest that, apart from a maintenance of the activity of the phagocytes under the conditions which come into consideration here, it would be impracticable to compare the results of experiments instituted in succession with one and the same quantum of washed corpuscles, or to compare the phagocytic power of different bloods unless in the case where these were withdrawn from the organism simultaneously.

A number of experiments undertaken with a view of obtaining information with regard to the point here raised have shown us that the phagocytic power is well maintained under the circumstances of our experiments. Even after the lapse of 3 days (our observations have not extended beyond this limit) the phagocytic power has not declined to less than one-half or one-third of that of the blood freshly drawn. We have found no indication of a variation within the space of a few hours.

These preliminary points having been dealt with, we may pass to the consideration of the problem to which attention was directed in the opening paragraph of this paper.

DOES THE SUBSTITUTION OF ANOTHER MEDIUM FOR THE (CITRATED)  
BLOOD PLASMA WHICH BATHES THE CORPUSCLES EXERT AN  
INFLUENCE ON PHAGOCYTOSIS ?

1. *Comparative Experiments with Citrated Plasma and Citrated Serum  
(obtained Respectively as Described in Connection with Procedures 2 and 3).*

EXPERIMENT 1.

A.—S. R. D.'s plasma, 3 vols. ; staphylococcus suspension, 1 vol. ;  
A. E. W.'s corpuscles, 3 vols.

|                                                                                                                  |     |     |     |      |        |
|------------------------------------------------------------------------------------------------------------------|-----|-----|-----|------|--------|
| Tube 1.—Phagocytic power (obtained by averaging the<br>number of staphylococci ingested by 20<br>P.W.B.C.) ..... |     |     |     | 34·6 | } 34·1 |
| Tube 2.—                                                                                                         | Do. | do. | do. | 33·6 |        |

B.—S. R. D.'s serum, 3 vols. ; staphylococcus suspension, 1 vol. ;  
A. E. W.'s corpuscles, 3 vols.

|                                                  |     |     |     |      |        |
|--------------------------------------------------|-----|-----|-----|------|--------|
| Tube 1.—Phagocytic power (elicited as above) ... |     |     |     | 35·6 | } 34·7 |
| Tube 2.—                                         | Do. | do. | ... | 33·8 |        |

EXPERIMENT 2.

A.—A. E. W.'s plasma, 3 vols. ; staphylococcus suspension, 1 vol. ;  
A. E. W.'s corpuscles, 3 vols.

|                                                  |     |     |     |      |        |
|--------------------------------------------------|-----|-----|-----|------|--------|
| Tube 1.—Phagocytic power (elicited as above) ... |     |     |     | 31·2 | } 33·6 |
| Tube 2.—                                         | Do. | do. | ... | 36·0 |        |

B.—A. E. W.'s serum, 3 vols. ; staphylococcus suspension, 1 vol. ;  
A. E. W.'s corpuscles, 3 vols.

|                                                  |     |     |     |      |        |
|--------------------------------------------------|-----|-----|-----|------|--------|
| Tube 1.—Phagocytic power (elicited as above) ... |     |     |     | 31·2 | } 32·1 |
| Tube 2.—                                         | Do. | do. | ... | 33·0 |        |

It is clear that the phagocytic power is uninfluenced by the sub-  
stitution of serum for plasma.

2. *Comparative Experiments with Ordinary (Uncitrated) Serum Unheated  
and Heated for 10—15 min. to 60—65° C. and then cooled.*

EXPERIMENT 1.

A.—A. E. W.'s unheated serum, 3 vols. ; staphylococcus suspension,  
1 vol. ; A. E. W.'s corpuscles, 3 vols.

|                                                                                     |     |     |     |      |   |
|-------------------------------------------------------------------------------------|-----|-----|-----|------|---|
| Tube 1.—Phagocytic power (bacteria in 20 P.W.B.C.<br>enumerated and averaged) ..... |     |     |     | 17·4 | } |
| Tube 2.—                                                                            | Do. | do. | ... | 19·8 |   |

*B.*—A. E. W.'s *heated serum*, 3 vols. ; staphylococcus suspension, 1 vol. ; A. E. W.'s corpuscles, 3 vols.

*Tube 1.*—Phagocytic power (bacteria in 52 P.W.B.C. enumerated and averaged) ..... 0·6

*Tube 2.*—Phagocytic power (bacteria in 46 P.W.B.C. enumerated and averaged)..... 3·4

#### EXPERIMENT 2.

*A.*—S. R. D.'s *unheated serum*, 3 vols. ; staphylococcus suspension 1 vol. ; S. R. D.'s corpuscles, 3 vols.

*Tube 1.*—Phagocytic power (bacteria in 20 P.W.B.C. enumerated and averaged) ..... 18·5

*Tube 2.*—Phagocytic power (bacteria in 22 P.W.B.C. enumerated and averaged) ..... 16·0

*B.*—S. R. D.'s *heated serum*, 3 vols. ; staphylococcus suspension, 1 vol. ; S. R. D.'s corpuscles, 3 vols.

*Tube 1.*—Phagocytic power (bacteria in 29 P.W.B.C. counted and averaged) ..... 1·5

*Tube 2.*—Phagocytic power (bacteria in 46 P.W.B.C. counted and averaged) ..... 1·8

#### EXPERIMENT 3.

*A.*—A. E. W.'s *unheated serum*, 3 vols. ; staphylococcus suspension, 1 vol. ; A. E. W.'s corpuscles, 3 vols.

*Tube 1.*—Phagocytic power (bacteria in 9 P.W.B.C. counted and averaged) ..... 25·4

*Tube 2.*—Phagocytic power (bacteria in 18 P.W.B.C. counted and averaged) ..... 16·0

*B.*—A. E. W.'s *heated serum*, 3 vols. ; staphylococcus suspension, 1 vol. ; A. E. W.'s corpuscles, 3 vols.

*Tube 1.*—Phagocytic power (bacteria in 20 P.W.B.C. counted and averaged) ..... 0

*Tube 2.*—      Do.                      do.                      do.                      0

#### EXPERIMENT 4.

*A.*—S. R. D.'s *unheated serum*, staphylococcus suspension and corpuscles in the same proportions as before.

Phagocytic power (bacteria in 15 P.W.B.C. counted and averaged) ..... 15·7



*B.*—S. R. D.'s *heated serum*, *staphylococcus* suspension, and *corpuscles* in the same proportions as before.

Phagocytic power (bacteria in 45 P.W.B.C. counted and averaged) ..... 0.2

These experiments show that we must ascribe an important *role* to the blood fluids in connection with phagocytosis.

For the alternative assumption, the supposition, to wit, that inhibiting elements are developed in the serum during the process of heating, is rebutted by the results of a series of control experiments, which showed that the phagocytes display no greater activity in a medium of physiological salt solution than in a medium of heated serum.

It is further rebutted by the circumstance that the activity of phagocytosis falls off at the same rate when the unheated serum is diluted with salt solution as when it is diluted with heated serum.

The experiment whose results are tabulated below illustrates this last point.

*Results of a Comparison made between the Activating Power of (a) Unheated Serum diluted in Heated Serum, and (b) Unheated Serum diluted in Physiological Salt Solution.*

In each case 3 vols. of serum dilution were mixed with 1 vol. of *staphylococcus* suspension and 3 vols. of washed corpuscles.

| Dilution in which the unheated serum was employed. | Average phagocytic power of the P.W.B.C. in the case where the unheated serum was diluted with previously heated serum. | Average phagocytic power of the P.W.B.C. in the case where the unheated serum was diluted with physiological salt solution. |
|----------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------|
| 3-fold                                             | ..                                                                                                                      | 34.2                                                                                                                        |
| 6-fold                                             | 27.4                                                                                                                    | 27.2                                                                                                                        |
| 12-fold                                            | 23.1                                                                                                                    | 30.5                                                                                                                        |
| 24-fold                                            | 20.6                                                                                                                    | 24.8                                                                                                                        |
| 48-fold                                            | 5.0                                                                                                                     | 4.95                                                                                                                        |
| 96-fold                                            | ..                                                                                                                      | 0.8                                                                                                                         |
| 192-fold                                           | ..                                                                                                                      | 0.6                                                                                                                         |

It is clear that we may conclude that the heated serum, like the salt solution, acts merely as an inert diluent, and that we may, in referring to such heated serum, characterise it simply as "inactivated serum." It is further clear that we may legitimately ascribe the small amount of phagocytosis which occurred in Experiments 1, 2, and 4 *supra*, to the presence of a residuum of unheated serum, which the washing operations had failed to separate from the corpuscles.

DO THE BLOOD FLUIDS CO-OPERATE IN PHAGOCYTOSIS BY EXERTING A DIRECT "STIMULATING" EFFECT UPON THE PHAGOCYTES, OR BY EFFECTING A MODIFICATION IN THE BACTERIA ?

The following experiments were instituted with a view to elucidating the problem as to the nature of the activating influence exercised by the blood fluids. It will be seen that a comparison is in each case instituted between serum inactivated (by heating) before it came in contact with either bacteria or white corpuscles, and serum inactivated after it had come in contact with the bacteria, but before it had come in contact with the white corpuscles:—

EXPERIMENT 1.

A.—S. R. D.'s *inactivated* serum, 3 vols. ; staphylococcus suspension (previously heated to 60° C. for 15 minutes and cooled), 1 vol. ; S. R. D.'s corpuscles, 3 vols.

|                                                                               |      |
|-------------------------------------------------------------------------------|------|
| Tube 1.—Phagocytic power (bacteria in 20 P.W.B.C. counted and averaged) ..... | 3·4  |
| Tube 2.—Do. do. ....                                                          | 3·35 |

B.—S. R. D.'s *unheated* serum, 3 vols. ; digested at 37° C. for 15 minutes, with 1 vol. of staphylococcus suspension, then heated to 60° C. for 15 minutes and cooled.

4 vols. of the above mixed with 3 vols. of S. R. D.'s corpuscles.

|                                                                               |      |
|-------------------------------------------------------------------------------|------|
| Tube 1.—Phagocytic power (bacteria in 20 P.W.B.C. counted and averaged) ..... | 27·5 |
| Tube 2.—Do. do. ....                                                          | 28·9 |

EXPERIMENT 2.

A.—A. E. W.'s *inactivated* serum, 3 vols. ; staphylococcus suspension, 1 vol. ; digested together for 15 minutes at 37° C., then heated for 10 minutes to 60° C. and cooled.

4 vols. of the above mixed with 3 vols. of S. R. D.'s corpuscles.

|                                                                               |     |
|-------------------------------------------------------------------------------|-----|
| Tube 1.—Phagocytic power (bacteria in 20 P.W.B.C. counted and averaged) ..... | 4·0 |
| Tube 2.—Do. do. ....                                                          | 3·2 |

B.—A. E. W.'s *unheated* serum, 3 vols. ; staphylococcus suspension, 1 vol. ; digested together for 15 minutes at 37° C., then heated for 10 minutes to 60° C. and cooled.

4 vols. of the above added to 3 vols. of S. R. D.'s corpuscles.

|                                                                               |    |
|-------------------------------------------------------------------------------|----|
| Tube 1.—Phagocytic power (bacteria in 24 P.W.B.C. counted and averaged) ..... | 33 |
| Tube 2.—Phagocytic power (bacteria in 19 P.W.B.C. counted and averaged) ..... | 36 |

## EXPERIMENT 3.

A.—S. R. D.'s *inactivated* serum, 3 vols. ; staphylococcus suspension (previously heated to 75° C. and cooled), 1 vol. ; digested together for 15 minutes at 37° C.

4 vols. of the above added to 3 vols. of S. R. D.'s corpuscles.

Phagocytic power (bacteria in 30 P.W.B.C. counted and averaged) ..... 4·2

B.—S. R. D.'s *unheated* serum, 3 vols. ; staphylococcus suspension (previously heated to 75° C. and cooled), 1 vol. ; digested together for 15 minutes at 37° C., then heated for 10 minutes to 60° C., and cooled.

4 vols. of the above added to 3 vols. of corpuscles.

Tube 1.—Phagocytic power (bacteria in 15 P.W.B.C. counted and averaged) ..... 28·2

Tube 2.— Do. do. 31·0

We have here conclusive proof that the blood fluids modify the bacteria in a manner which renders them a ready prey to the phagocytes.

We may speak of this as an "*opsonic*" effect (opsono—I cater for ; I prepare victuals for), and we may employ the term "*opsonins*" to designate the elements in the blood fluids which produce this effect.

DOES THE UNHEATED SERUM CONTAIN, IN ADDITION TO ELEMENTS WHICH RENDER THE BACTERIA MORE LIABLE TO PHAGOCYTOSIS (OPSONINS), ALSO ELEMENTS WHICH DIRECTLY STIMULATE THE PHAGOCYTES (STIMULINS) ?

We have sought to elucidate this question by three separate methods.

In a first series of experiments, we experimented with staphylococci which had been exposed to high temperatures (115° C.) with the design of rendering them insusceptible to the opsonic power of the blood fluids. Our expectations from this method—expectations based on the fact that we had noticed that typhoid bacilli acquired, when heated to over 70° C., a resistance to the bacteriolytic effect of the blood fluids—were unrealised. We found that the quantitative differences between the phagocytosis in heated and unheated serum respectively were not less in the case of staphylococci which had been exposed to a temperature of 115° C., than in the case of staphylococci which had not been subjected to high temperatures.

In a second series of experiments we substituted for suspensions of staphylococci suspensions of particles, which we assumed would be *uninfluenced* by the opsonic power of the blood. The results of these

experiments, conducted both with carmine particles and with Indian ink, were inconclusive by reason of the circumstance that we were not able to obtain any satisfactory enumerations. An impression was, however, left on our minds that phagocytosis was in every case more active in unheated than in the heated serum.

A third method of experimentation was then resorted to. In a first operation we mixed and digested together at blood heat a suspension of staphylococci and unheated serum. After allowing what we supposed would be a sufficient interval for the exhaustion of the effect of the serum upon the bacteria, we divided the mixture into two portions. While the first of these portions was mixed with the corpuscles without undergoing any further treatment, the other was heated to 60° C., and cooled before it was so mixed. In each case the phagocytic power exerted was greater in the case where the heating was omitted, and the differences were not less marked where the serum had been digested with the bacteria for 50 minutes and 1 hour respectively than in the case where it had been digested with these only for 15 minutes.

These results are ambiguous.

The question as to whether the blood fluids contain, in addition to opsonins, also an element which directly stimulates the phagocytes, remains for the present unsolved.

The third series of experiments, which has just been adverted to, is subjoined :—

#### EXPERIMENT 1.

S. R. D.'s serum, 3 vols. ; digested with staphylococcus suspension, 1 vol., for 15 minutes at 37° C.

A.—4 vols. of the above mixture heated to 60° C. for 15 minutes, then cooled and added to 3 vols. of S. R. D.'s corpuscles.

Tube 1.—Phagocytic power (bacteria in 16 P.W.B.C. enumerated and averaged) ..... 22·0

Tube 2.—Phagocytic power (bacteria in 31 P.W.B.C. enumerated and averaged) ..... 20·7

B.—4 vols. of the above mixture added directly to 3 vols. of S. R. D.'s corpuscles.

Tube 1.—Phagocytic power (bacteria in 16 P.W.B.C. counted and averaged) ..... 27

Tube 2.—Phagocytic power (bacteria in 28 P.W.B.C. counted and averaged) ..... 28

#### EXPERIMENT 2.

S. R. D.'s unheated serum, 3 vols. ; digested with staphylococcus suspension, 1 vol for 50 minutes at 37° C.

*A.*—4 vols. of the above mixture heated to 60° C. for 20 minutes, then cooled and added to 3 vols. of S. R. D.'s corpuscles.

|                                                                                          |      |
|------------------------------------------------------------------------------------------|------|
| <i>Tube 1.</i> —Phagocytic power (bacteria in 20 P.W.B.C. enumerated and averaged) ..... | 13·5 |
| <i>Tube 2.</i> —Do. do.                                                                  | 17·1 |

*B.*—4 vols. of the above mixture added directly to 3 vols. S. R. D.'s corpuscles.

|                                                                         |      |
|-------------------------------------------------------------------------|------|
| <i>Tube 1.</i> —(Bacteria in 15 P.W.B.C. enumerated and averaged) ..... | 40·6 |
| <i>Tube 2.</i> —Do. do.                                                 | 44·5 |

### EXPERIMENT 3.

S. R. D.'s unheated serum, 3 vols.; 1 vol. of staphylococcus suspension; digested together 1 hour at 37° C.

*A.*—4 vols. of the above mixture heated to 60° C. for 10 minutes, cooled and added to 3 vols. of S. R. D.'s corpuscles.

|                                                                                          |      |
|------------------------------------------------------------------------------------------|------|
| <i>Tube 1.</i> —Phagocytic power (bacteria in 16 P.W.B.C. enumerated and averaged) ..... | 15·1 |
|------------------------------------------------------------------------------------------|------|

*B.*—4 vols. of the above mixture added directly to 3 vols. of S. R. D.'s corpuscles.

|                                                                                       |      |
|---------------------------------------------------------------------------------------|------|
| <i>Tube 1.</i> —Phagocytic power (bacteria in 16 P.W.B.C. counted and averaged) ..... | 22·1 |
|---------------------------------------------------------------------------------------|------|

In conclusion we would briefly refer to the following points:—

The opsonic power of the blood fluids disappears gradually on standing, even when the serum is kept in a sealed capsule sheltered from the light.

After 5 or 6 days we have found the opsonic power of the serum kept under these conditions to stand at little more than half of what it was originally.

The opsonic power of the blood fluids is but little impaired by the action of heat until these have been exposed to temperatures above 50° C. The following are the results of a typical experiment:—Phagocytic power obtained with the serum before exposure to heat, 12·7; with the same serum heated for 10 minutes to 45° C., 13·1; with the same serum heated for 10 minutes to 50° C., 10·2; with the same serum heated for 10 minutes to 55° C., 5·7.

The opsonic power of the serum is diminished when this last has been digested with typhoid bacteria. This "anti-opsonic" effect may be compared with the "anti-bactericidal" effect\* obtained on digesting the serum with typhoid or cholera cultures.

\* Wright and Windsor, 'Journal of Hygiene,' vol. 2, No. 4, Oct., 1902.

The opsonic power of the blood fluids is diminished while the phagocytic capacity of the W.B.C. is preserved when the blood fluids and corpuscles are separately digested with Daboia venom. In the anti-opsonic effect, exerted by the venom on the blood fluids, we have probably the explanation of the reduced resistance to septic invasion which supervenes upon viper bites.

It would seem probable that the bacteriolytic, bactericidal, and bacterio-opsonic effects exerted by the blood fluids are each in their degree manifestations of a digestive power exerted by the blood fluids on bacteria brought into contact with them.

Lastly, a fact which has a practical importance in connection with the study of immunity may be adverted to. It will be manifest that we have not exhausted the study of a condition of immunity when we have measured the phagocytic power of the white corpuscles, and the agglutinating, bacteriolytic, and bactericidal powers of the blood fluids. We must, in connection with these last, take into consideration also the opsonic effect.

A concrete example may be added to show the kind of elucidation which may be gained from an inquiry which takes into consideration also the factor last mentioned.

The condition of immunity to staphylococcus which can be induced in patients unduly susceptible to staphylococcus infections, by the inoculation of properly adjusted doses of a sterilised staphylococcus culture is, as was shown by one of us, associated with an increase of the phagocytic power\* of the white blood corpuscles, and is unaccompanied by any development of a bactericidal power in the blood fluids.

The result of the subjoined blood examinations undertaken upon a patient who had been subjected to two successive therapeutic inoculations of a sterilised staphylococcus culture, suggests that the increased phagocytic power may depend upon an increase in the opsonic power of the blood fluids.

*A.*—A. E. W.'s serum, 3 vols.; staphylococcus suspension, 1 vol.; and A. E. W.'s washed corpuscles, 3 vols.

*Tube 1.*—Phagocytic power (bacteria in 20 P.W.B.C. counted and averaged) ..... 17·4

*Tube 2.*—Phagocytic power (bacteria in 26 P.W.B.C. counted and averaged) ..... 19·9

*B.*—The patient's serum, 3 vols.; staphylococcus suspension, 1 vol.; the patient's washed corpuscles, 3 vols.

*Tube 1.*—Phagocytic power (bacteria in 15 P.W.B.C. counted and averaged) ..... 35

*Tube 2.*—Do. do. do. do. ..... 36

\* \* \* *'Lancet,' March 29, 1902.*

C.—The patient's serum, 3 vols. ; staphylococcus suspension, 1 vol. ;  
A. E. W.'s washed corpuscles, 3 vols.

|                                                   |     |     |
|---------------------------------------------------|-----|-----|
| Tube 1.—Phagocytic power (bacteria in 15 P.W.B.C. |     |     |
| counted and averaged) .....                       |     | 30  |
| Tube 2.—                                          | Do. | do. |
|                                                   |     | 26  |

“The Magnetic Expansion of some of the less Magnetic Metals.”  
By P. E. SHAW, B.A., D.Sc. Communicated by Professor  
J. H. POYNTING, F.R.S. Received May 22,—Read June 18,  
1903.

1. Abundant research has been made on the magnetic expansion of iron, nickel, and cobalt, notably as regards the exact relation between field ( $H$ ) and expansion per unit length ( $\delta l/l$ ), by S. Bidwell\* and H. Nagaoka.† Bismuth also has been investigated by Bidwell, C. G. Knott, Van Aubel, and A. P. Wills. But there seems to be no recorded research on any materials other than the four mentioned.

Outside the ferro-magnetic group bismuth has the largest susceptibility ( $k$ ) of any substance ; and the tacit assumption seems to have been made that if bismuth shows no change in length as the field varies, it is vain to look for it in less susceptible metals.

But in the case of the ferro-magnetics there is no direct relation between  $k$  and  $\delta l/l$ . Thus, iron has maximum susceptibility six times as much as nickel, and yet expands far less for any known field.

Again, cobalt has maximum susceptibility one-eighth of that of iron, yet expands about as much.

There being, therefore, no close relation between susceptibility and magnetic expansion, it seems possible that there may be appreciable movement for large fields in the case of metals outside the ferro-magnetic group. This paper gives an account of tests applied to bismuth, silver, aluminium, copper, zinc, brass, bronze, lead, and tin. (Not much importance should be attached to the results for lead and tin owing to the softness of these metals ; they tend to work loose in their fittings at each end.) The work has taken from first to last nearly two years : the specimens have been repeatedly changed and the magnetic and measuring parts of the apparatus modified in various ways. In this way searching tests have been applied to the investigation.

For a long time it appeared (1) that all these metals contracted, the contraction being roughly proportional to the field, (2) that all the metals showed permanent magnetisation, on the hysteresis principle,

\* ‘Phil. Trans.’ A, 1888.

† ‘Phil. Mag.’ Jan., 1894.

just as was shown by Nagaoka\* for iron and nickel. But step by step these inferences have been proved to be fallacious, as greater care was taken in the exclusion of iron from the apparatus and in the exact setting of the rod symmetrical in the coil and free from mechanical connection with it. The final conclusion reached is that no true expansion, positive or negative, can be detected within the limits of the experiment.

2. The magnetic and length-measuring apparatus have been described in previous communications† and cannot easily be summarised intelligibly.

I am indebted to Mr. Schott (see the Note appended) for working out the value of the reduction factor  $\kappa$  in the expression

$$H = 4\pi N\gamma \cdot \kappa.$$

The ordinary expression  $H = 4\pi N\gamma$  requires modifying for such a short solenoid as the one used by me. The numerical calculation of the integrals in the note gives for  $\kappa$  the value 0.867.

The rods are cylinders, 19 cm. long, 6 mm. diameter (except bismuth and lead 12 mm. diameter).

The coil is 19 cm. long and has 3604 turns, hence  $N = 190$ .

Using the values of currents ( $\gamma$ ) below, we derive the corresponding value of field ( $H$ ), where  $H$  is the effective uniform field as expressed above.

|                          |      |       |      |      |      |      |      |      |      |
|--------------------------|------|-------|------|------|------|------|------|------|------|
| $\gamma$ (in ampères)... | 0.80 | 1.45  | 2.00 | 2.50 | 3.10 | 3.80 | 4.43 | 5.30 | 6.40 |
|                          | 7.70 | 9.25. |      |      |      |      |      |      |      |
| $H$ (c.g.s. units) ..    | 164  | 295   | 413  | 510  | 635  | 784  | 900  | 1090 | 1313 |
|                          | 1588 | 1906. |      |      |      |      |      |      |      |

These currents were read on an ammeter which was periodically calibrated. They were always applied gradually by using a sliding liquid resistance, vanishing to *nil*.

The coil was made somewhat short. This was done in order, with a given resistance in the windings, to concentrate the field on the rod.

Again, the rod occupied the whole length of the coil. It is customary when experimenting on a ferro-magnetic to build the core up of three parts, the ferro-magnetic occupying the central third of the length (where the field is practically uniform), whilst the two end thirds of the length are of brass. Here the assumption is made that brass itself undergoes no expansion. I could not proceed on this plan, for we have no certainty that any metal is neutral, *i.e.*, is quite free from magnetic expansion. So I decided to have the rod the same length as the coil and trust to calculations to obtain the mean effective

\* *Loc. cit.*

† Shaw and Laws, 'Electrician,' Feb., 1901, and Feb., 1902.



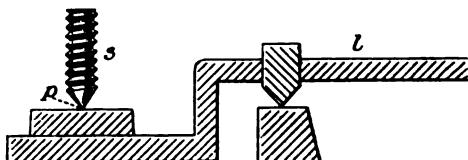
field throughout its length. In the present research it is immaterial if there be a small error in the calculated value of field; but it is essential that any expansion produced should be due to the specimen exclusively.

As regards the rod, we are not troubled by the demagnetising factor ( $N$ ) in the well-known expression for effective field,\*

$$H' = H - NI,$$

where  $I$  = magnetic intensity and  $H = 4\pi n\gamma$ . In the present instance since  $k$  is very small for all the metals in question,  $I$  becomes insensible

FIG. 1.



The electric micrometer was calibrated by using a simple electric micrometer† in the following way, which is accurate enough for present purposes. Suppose  $l$  is the last lever of the system of levers and  $p$  is the measuring point; we require to know how many divisions of the electric micrometer screw correspond to a known movement of  $p$ . Remove the coil and accessories which are above  $p$ , and bring screw of the simple micrometer down to  $p$ . When electric contact is completed take a reading of the graduated head of the screw  $s$ . Rotate so that the surfaces at  $p$  are separated by a known amount, say 4 microns. Then find out how much the screw of the electric micrometer has to be rotated to bring the surfaces together again and produce electric contact once more.

As a means of four results, 4 microns movement at  $p$  corresponds to 14,900 divisions on the electric micrometer screw, hence—

1 micrometer division corresponds to  $2.68 \times 10^{-8}$  cm., which (since the rod is 19 cm. long) is equivalent to  $1.4 \times 10^{-9}$  of the length of the rod.

Allowing for uncertainties in readings, I should say that three divisions on the scale represent the smallest difference that can be detected with certainty.

3. As seen above, the range of field was considerable and the upper limit high (1900 c.g.s.), while the measuring apparatus was very delicate.

\* Ewing's 'Magnetic Induction,' 2nd edition, p. 24.

† 'Phys. Rev.,' March, 1903.

Various strains, other than those for which we are looking, will be liable to occur, and to show themselves in the measuring apparatus, *e.g.*, due to (1) solenoidal suction of the coil on the end; (2) directive action of the earth's field on the magnetised coil; (3) attractive action on the coil of any iron in its neighbourhood.

It is very difficult to eliminate all such false strains. At first I worked with the coil attached to the lower end of the rod, counterpoising the coil to remove all strain from the rod. This method was employed by S. Bidwell,\* it obviates solenoidal suction and may on that account be useful with a ferro-magnetic core, but in my experience it was troublesome. I then placed the coil on a stand separate from the core and its supports, taking care to centre the rod in the coil. The coil and core must not come into contact or the small movements of the former will displace the latter.

A great deal of time was spent in finding out the best conditions of working; thousands of readings often apparently quite consistent for a long time were taken down. These readings varied from  $1 \times 10^{-6}$  cm. to  $1 \times 10^{-8}$  cm. But gradually, as the elimination of disturbing causes proceeded, the result in the case of every metal tried was found to be *nil*.

Bismuth was tested with special interest on account of the work already done on it.

S. Bidwell† recorded a small expansion, but later‡ he reported that although the field used was 1500 c.g.s., and the unit of measurement  $1/70,000,000$  of the length of the rod, yet no movement could be found.

No other attempt seems to have been nearly as searching as this last, although Knott,§ Van Aubel,|| and lately A. P. Wills¶ have also taken up the matter and record the same negative result.

After working with one specimen of bismuth, I had the material recast of somewhat less diameter, taking care to remove the surface, which might obtain impurities from the loam used in the casting. In both field and length measurement, the test which I have applied to bismuth appears to go further than any previous one, for, as shown above, the maximum field is 1900 c.g.s., and the smallest movement per unit length readable is  $\delta l/l = 4 \times 10^{-9}$  cm.

The metals used were obtained specially pure from Messrs. Johnson and Matthey; they were analysed for traces of iron by the sulphocyanide colour test. The following list shows the amount of iron in 10,000 parts of metal: bismuth, 0.88; silver, 1.0; tin, 0.1; aluminium, 72; zinc, 0.68; lead, 0.26; copper, 4.8; bronze, 7.0; brass, 4.0.

4.—(u) It has generally been supposed that a small trace of iron in

\* *Loc. cit.*

† 'Phil. Trans.,' A, 1888.

‡ 'Nature,' July, 1899.

§ 'Nature,' June, 1899.

|| 'Nature,' Aug., 1899.

¶ 'Phys. Rev.,' July, 1902.

a metal would produce magnetic expansion on its own account which would mask any small expansion due to the metal. From the analyses above, we may test this hypothesis.

Aluminium, silver, bronze, copper and brass all have more iron than 1 in 10,000 parts. Now in a field of 1900 c.g.s., the value of  $\delta/l$  for iron is about  $-4 \cdot 10^{-5}$ ; assuming simple superposition of the expansions of the two ingredients, then 1 of iron in 10,000 of metal should produce a value for  $\delta/l$  equal to  $-4 \times 10^{-9}$ .

But, as shown above, this movement is readable on the electric micrometer. In aluminium, and even in brass and copper, the impurity should have produced quite a large movement in my apparatus.

It would be interesting to examine the relation of the amount of iron in a specimen to the magnetic expansion. My experiments certainly do not confirm the simple superposition theory.

(b) At one time it was not uncommon for writers on magnetic expansion to deduct a contraction  $e = B^2/8\pi M$  from the whole expansion observed, this being supposed to be always caused by the Maxwell stress in the magnetised substance.

But this course has been shown by Dr. Chree to be unjustifiable.\*

In these experiments, putting  $B = H = 1900$  c.g.s. and giving  $M$  the value  $10''$  c.g.s., we have  $e = 2 \times 10^{-6}$  cm. for each unit length of specimen, or for the rods used (19 cm. long)  $e = 4 \times 10^{-5}$  cm., roughly.

Any such quantity would be easily detected by the apparatus. Hence the conclusion is that the stress does not act wholly, if at all, on the matter. If only one ten-thousandth of the stress acted directly on the matter the effect would have been perceptible.

The negative results of these experiments, like those of Sir O. Lodge,† seem to show that the mechanical connection between matter and ether, if existent, is inappreciable by our present methods.

I have pleasure in acknowledging my obligation to the Royal Society for the Government grant made to me in 1901, by which the cost of this research has been defrayed.

\* See letters by Chree and others, 'Nature,' Jan., 1896.

† 'Phil. Trans.,' A, 1897.

*Note by G. A. SCHOTT, B.A., B.Sc.*

*Calculation of the Elongation, due to the Magnetic Field, of the Cylindrical Bars.*

The dimensions of Dr. Shaw's apparatus are as follows :—

|                                  |                                    |
|----------------------------------|------------------------------------|
| Length of solenoid and bar ..... | (2 <i>l</i> ) = 19 cm.             |
| Mean radius of solenoid .....    | ( <i>a</i> ) = 2·75 cm.            |
| Depth of winding .....           | (2 <i>c</i> ) = 2·40 cm.           |
| Number of layers.....            | (2 <i>p</i> ) = 22                 |
| „ turns per layer .....          | ( <i>n</i> ) = 164                 |
| Distance between layers .....    | ( <i>h</i> ) = 4/35 cm.            |
| Radius of bar .....              | ( <i>b</i> ) = from 0·3 to 0·6 cm. |

Use cylindrical co-ordinates (*z*, *ρ*) where *O z* is the axis of the bar and the origin is at the centre.

Let the axial and radial components of the magnetic force (*H*), due to the solenoid, be *Z*, *R*, and those due to the induced magnetisation *H'*, *Z'*, *R'*.

*R R'* are of order *ρ*, and inside the bar are small compared with *Z*; they give terms in the strain of order *ρ*<sup>2</sup>, which are less than 1 per cent. of the whole and may be neglected. In the same way there are terms of order *ρ*<sup>2</sup> in *Z*, which can be neglected. Thus we may for our purpose regard the magnetic force inside the bar as axial and constant over any cross section, but variable from end to end.

The intensity of magnetisation is given by  $I = k(H + H')$ . The volume density of magnetism is  $\text{div. } I = (H + H') \text{ div. } k + k \text{ div. } H'$ , since  $\text{div. } H = 0$ .

For all the metals used by Dr. Shaw, *k* is exceedingly small (at most 10<sup>-5</sup>), and its square may be neglected.  $\text{Div. } k$  involves the differential coefficients of *k* with respect to the strains as well as space-variations of the strains. The former, though they may be large compared to *k*, yet are small absolutely; the latter also are small; hence,  $\text{div. } k$  is negligible. Since *H'* is of order *I*, the volume density of magnetism is of order *k*<sup>2</sup> and negligible. The induced magnetism is confined to the surface of the bar, and the force *H'*, being of order *k*, may be neglected.

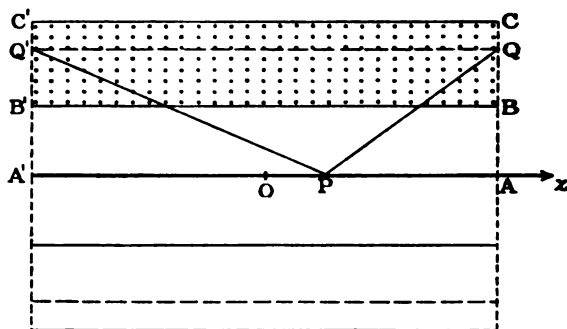
Thus we need only take account of the component *Z*.

We shall require the mean values of *Z* and *Z*<sup>2</sup>, say  $\bar{Z}$  and  $\bar{Z^2}$ .

The figure gives a meridian section. *A'A* is the axis, *BCC'B'* the section of the upper half of the solenoid, *QQ'* the section of a layer of wire of radius *r*.

As we neglect variations of *Z* across the section of the bar, we need only consider its value at a point *P* (*z*) on the axis.

FIG. 2.



By a well-known formula the magnetic force ( $\Delta Z$ ), due to the layer  $QQ'$  carrying current  $\gamma$ , is given by

$$\Delta Z = \frac{\pi n \gamma}{l} \left[ \frac{l-z}{\sqrt{[(l-z)^2 + r^2]}} + \frac{l+z}{\sqrt{[(l+z)^2 + r^2]}} \right].$$

Here

$$r = a - c + qh, \quad q = 0, 1, \dots, 20, 21.$$

Maclaurin's summation formula gives

$$\Sigma f(r) = \frac{2c+h}{h} \left\{ f(a) + \frac{c(c+h)}{6} f''(a) \right\} = 22 \left\{ f(a) + 0.184 c^2 f''(a) \right\},$$

where terms of order  $\frac{h^2}{6} f''(a) = \frac{c^2}{660} f''(a)$  have been neglected.

The total number of ampère turns in the solenoid is  $22n\gamma$ , and the number per centimetre is  $22n\gamma/2l$ ; let the magnetic force inside an infinitely long solenoid with the same number of ampère turns per centimetre be  $H$ , then  $H = \frac{4\pi}{2l} \frac{22n\gamma}{2} = 4\pi N\gamma$ .

Maclaurin's formula gives for the actual magnetic force

$$\begin{aligned} Z = \Sigma \Delta Z = \frac{1}{2} H \left[ \frac{l-z}{\sqrt{[(l-z)^2 + a^2]}} \left\{ 1 - 0.184 \frac{c^2}{(l-z)^2 + a^2} \right. \right. \\ \left. \left. + 0.552 \frac{a^2 c^2}{\{(l-z)^2 + a^2\}^2} \right\} \right. \\ \left. + \frac{l+z}{\sqrt{[(l+z)^2 + a^2]}} \left\{ 1 - 0.184 \frac{c^2}{(l+z)^2 + a^2} \right. \right. \\ \left. \left. + 0.552 \frac{a^2 c^2}{\{(l+z)^2 + a^2\}^2} \right\} \right] \dots \dots (1). \end{aligned}$$

Now we have  $2l = 19$ ,  $a = 2.75$ ,  $c = 1.20$ , so that

$$\frac{a}{l} = 0.290, \quad \frac{a}{\sqrt{(4l^2 + a^2)}} = 0.143, \quad \frac{c^2}{a^2} = 0.192.$$

Also

$$\frac{1}{2l} \int_{-l}^l \frac{(l-z) dz}{\{(l-z)^2 + a^2\}^{n+1}} = \frac{1}{2l} \int_{-l}^l \frac{(l+z) dz}{\{(l+z)^2 + a^2\}^{n+1}} \\ = \frac{a}{2l} \frac{1}{(2n-1)a^{2n}} \left\{ 1 - \left( \frac{a}{\sqrt{(4l^2 + a^2)}} \right)^{2n-1} \right\}.$$

Hence from (1)

$$\bar{Z} = H (0.866 - 0.184 \times 0.192 \times 0.145 \times 0.857 + 0.552 \times 0.192 \times 0.145 \\ \times 0.332 = 0.867 \cdot H.$$

Again, (1) gives, after simple algebraic transformations,

$$Z^2 = H^2 \left[ 0.500 - 0.268 \frac{a^2}{(l-z)^2 + a^2} + 0.071 \frac{a^4}{\{(l-z)^2 + a^2\}^2} \right. \\ \left. - 0.024 \frac{a^6}{\{(l-z)^2 + a^2\}^3} \right. \\ \left. - 0.268 \frac{a^2}{(l+z)^2 + a^2} + 0.071 \frac{a^4}{\{(l+z)^2 + a^2\}^2} \right. \\ \left. - 0.024 \frac{a^6}{\{(l+z)^2 + a^2\}^3} \right. \\ \left. + \frac{l^2 - z^2}{\sqrt{[(l-z)^2 + a^2]} \sqrt{[(l+z)^2 + a^2]}} \right. \\ \left. \left\{ 0.500 - 0.018 \frac{a^2}{(l-z)^2 + a^2} + 0.053 \frac{a^4}{\{(l-z)^2 + a^2\}^2} \right. \right. \\ \left. \left. - 0.018 \frac{a^2}{(l+z)^2 + a^2} + 0.053 \frac{a^4}{\{(l+z)^2 + a^2\}^2} \right\} \right],$$

where terms in  $a^4$  have been neglected.

$\bar{Z}^2$  involves the following integrals:—

$$\frac{1}{2l} \int_{-l}^l \left[ \frac{dz}{\{(l-z)^2 + a^2\}^{n+1}} + \frac{dz}{\{(l+z)^2 + a^2\}^{n+1}} \right],$$

and

$$\frac{1}{2l} \int_{-l}^l \left[ \frac{1}{\{(l-z)^2 + a^2\}^{n+1}} + \frac{1}{\{(l+z)^2 + a^2\}^{n+1}} \right] \frac{(l^2 - z^2) dz}{\sqrt{[(l-z)^2 + a^2]} \sqrt{[(l+z)^2 + a^2]}}.$$

Call them  $I_n$ ,  $J_n$ .

In  $I_n$  put  $l \pm z = a \cot \theta$ ; then

$$I_n = \frac{a}{l} \frac{1}{a^{2n}} \int_{\tan^{-1} a/2l}^{\frac{1}{2}\pi} \sin^{2n-2} \theta \cdot d\theta \\ = \frac{0.290}{a^{2n}} \left[ \frac{1 \cdot 3 \cdot \dots \cdot (2n-3)}{2 \cdot 4 \cdot \dots \cdot (2n-2)} \frac{\pi}{2} - \frac{1}{2n-1} \left( \frac{a}{2l} \right)^{2n-1} \right], \text{ approximately.}$$

Thus

$$I_1 = \frac{0.414}{a^2}, \quad I_2 = \frac{0.228}{a^4}, \quad I_3 = \frac{0.171}{a^6}.$$

In  $J_n$  put  $z = \sqrt{(l^2 + a^2)} \frac{\cos(\theta + \alpha)}{\cos(\theta - \alpha)}$ , where  $\alpha$  is defined by  $\tan 2\alpha = \frac{a}{l}$ ; also let  $t = \tan \alpha$ .

With the above values of  $a/l$  we have  $\alpha = 8^\circ 5'$ ,  $t = 0.142$ .

Clearly  $t^n$  is negligible except where it is divided by  $\cos \theta$  or  $\sin \theta$ , which become of order  $t$  at one or other limit. This substitution gives

$$\begin{aligned} J_n &= \frac{1}{a^{2n}} \frac{2t}{(1+t^2)^{n-1}} \int_a^{\frac{1}{2}\pi - \alpha} (1+t^{2n} \sec^{2n} \theta) (\cos \theta + t \sin \theta)^{2n-2} (\sin \theta - t \cos \theta) d\theta \\ &= \frac{1}{a^{2n}} \frac{2t \sqrt{(1+t^2)}}{2n-1} [1+t^{2n} \cdot (1+t^2)^n - 1 + (1+t^2)^n] \left( \frac{2t}{1+t^2} \right)^{2n-1} \\ &\quad + \frac{2nt^{2n}}{(1+t^2)^{2n-1/2}} \int_a^{\frac{1}{2}\pi - \alpha} (1+t \tan \theta)^{2n-1} \sec \theta \tan \theta d\theta, \end{aligned}$$

whence

$$J_0 = 1.484, \quad J_1 = \frac{0.242}{a^2}, \quad J_2 = \frac{0.097}{a^4} \dots$$

Hence we get

$$\begin{aligned} \bar{Z}^2 &= H^2 [0.500 - 0.268 \cdot a^2 I_1 + 0.071 \cdot a^4 I_2 - 0.024 a^6 I_3 \\ &\quad + 0.250 \cdot J_0 - 0.018 \cdot a^2 J_1 + 0.053 \cdot a^4 J_2] \\ &= 0.77 \cdot H^2. \end{aligned}$$

Lastly, (1) gives the values at the ends of the bar, say  $Z_l$  and  $Z_r$ . Resuming, we get the following values:—

$$\begin{aligned} \bar{Z} &= 0.867H, & Z_l &= 0.495H, \\ \bar{Z}^2 &= 0.77H^2, & Z_l^2 &= 0.245H^2. \end{aligned}$$


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"On the Measurement of the Pressure Coefficient of Oxygen, at Constant Volume, and different Initial Pressures." By WALTER MAKOWER, B.Sc., and HENRY R. NOBLE, B.Sc. Communicated by SIR WILLIAM RAMSAY, K.C.B., F.R.S. Received June 26, 1903.

*The Pressure Coefficient of Oxygen.*

1. *Introduction.*—Travers and Jaqueroed have recently carried out a series of measurements of the pressure coefficients of hydrogen and helium, and, in conjunction with Senter, have applied their results to the measurement of the vapour pressures of liquid oxygen and liquid hydrogen on the constant volume helium and hydrogen scales.\* At the conclusion of this research Dr. Travers suggested that we should make an attempt to determine the pressure coefficient of oxygen, which seemed to present those peculiar difficulties which are always associated with measurements involving the observation of mercury surfaces in contact with this gas. The apparatus employed has been previously described by Travers and Jaqueroed.†

2. *Previous Determinations.*—Regnault attempted to measure the pressure-coefficient of oxygen, but failed to obtain concordant results. He attributed his failure to the oxidation of the mercury in the manometer used to measure the pressure of the oxygen.‡

Von Jolly§ obtained the value 0·0036743 as the mean of eighteen observations at an initial pressure of about 760 mm. The individual observations are, however, very discordant, varying between 0·003680 and 0·003668.

3. *Preparation of the Oxygen and its Introduction into the Thermometer.*—The oxygen used was prepared by heating pure dry potassium permanganate. The oxygen so generated was passed over soda-lime and liquefied by passing it into a glass spiral immersed in liquid air. By lowering the vessel containing the liquid air, the oxygen could be allowed to boil off gently. In this way any trace of water vapour or other impurity which might have been present was completely removed.

The method of introducing the gas into the thermometer was precisely the same as that employed by Travers and Jaqueroed.||

The thermometer bulb, which at the beginning of the research contained helium, was exhausted to a high vacuum, along with the apparatus employed for generating the oxygen. The thermometer was then filled with pure oxygen and after a short time again exhausted.

\* 'Phil. Trans.,' A, vol. 200, p. 105.

† *Loc. cit.*

‡ 'Pogg. Ann.,' vol. 55, p. 391, 1842.

§ 'Pogg. Ann.,' Jubelband, p. 82, 1874.

|| *Loc. cit.*



This was repeated a second time, care being taken to admit just the quantity required to fill the apparatus to the pressure desired for taking observations. The instrument was then ready for use.

4. *Correction of Pressure Measurements for Parallax.*—The pressures exerted by the oxygen in the thermometer bulb were determined by measuring the height of a mercury column on a glass scale placed in front of it. In these circumstances errors due to parallax were apt to occur in the observations, unless great care was taken to bring the axis of the telescope into line with the top of the meniscus, or the glass point. This means that all readings were to be made at the intersection of the cross wires in the telescope. It was obviously impossible to read both point and meniscus at the centre simultaneously. A series of observations was therefore taken to determine in what way the apparent distance between a fixed graduation on the scale and the glass point (which was, of course, also fixed) varied with the position of the axis of the telescope. Care was always taken to adjust the telescope so as to make the parallax correction small and in most cases negligible; but when necessary the appropriate correction was applied.

5. *Calculation of Results.*—The pressure of the oxygen contained in the thermometer bulb was measured at the freezing point and at the boiling point of water.

The pressure coefficient ( $\alpha$ ) was deduced from the well-known definition

$$\alpha = \frac{P_\theta - P_0}{P_0 \theta},$$

where  $P_\theta$  is the pressure at the boiling point ( $\theta$ ) of steam on the Centigrade scale

and  $P_0$  that at the freezing point at a constant volume unity;

$P_\theta$  and  $P_0$  were calculated respectively from the formula:

$$P_0 = P \left( V_b + \frac{273t_s}{273 + t_s} + \frac{273v}{273 + t} \right)$$

$$P = P' \left( V_b' + \frac{\theta r_s'}{273 + t_s'} + \frac{\theta r'}{273 + t'} \right)$$

where  $P$  is the observed pressure at the ice point

and  $P'$  is that at the steam point,

$t_s$  and  $t_s'$  are the temperatures Centigrade at the ice and steam point observations respectively,

$t$  and  $t'$  are the temperatures of the dead space at the ice and steam point observations,

$V_b$  is the volume of the bulb at the ice point 94.2096 c.c.,

$V_b'$  is the volume of the bulb at the steam point 94.2096 (1 + 0.0000285 $\theta$ ),

$r_s$  is the volume of the stem (1031 c.c.),

$v$  is the volume of the dead space.

Correcting to a constant volume unity simplifies the calculation.

The volume of the dead space from a mark on the stem to a mercury meniscus of height 0.125 cm. in contact with the glass point was 0.3904 c.c.

To obtain the total volume of the dead space it is necessary to apply a correction to allow for the fact that the mercury meniscus was not brought exactly into contact with the glass point. This correction amounts to  $\pi r^2 \Delta$ , where  $\Delta$  is the distance between the surface of the mercury and the point and  $r$  is the radius of the tube (0.45 cm.). As the height of the mercury meniscus was found to vary considerably in the various experiments, it was necessary to introduce a further correction to allow for the variation of the volume of the dead space from this cause. Assuming the curvature of the meniscus to be constant, the correction to be added is  $\frac{1}{2}\pi r^2 (h' - h) - \frac{1}{8}\pi (h'^3 - h^3)$ , where  $h$  is the height at which the meniscus stood when the volume of the dead space was measured and  $h'$  is the height in the particular experiment.

6. *Method of Observation and Results.*—The measurements of pressure were taken in the manner adopted by Travers and Jaquero.<sup>\*</sup> Readings of the ice point and steam point were taken in most instances in alternate pairs, one series of observations being taken by each of us for each setting.

To illustrate the order of accuracy obtained, one series of observations is given in full, in the accompanying table. In the other series only the final corrected values are given.

### Details of Series III.

#### *Ice Point.*

| Observed pressure in millimetres corrected. | Volume of dead space in c.c. | Temperature centigrade of dead space. | Temperature centigrade of stem. | P <sub>o</sub> . | Mean P <sub>o</sub> . |
|---------------------------------------------|------------------------------|---------------------------------------|---------------------------------|------------------|-----------------------|
| 707.77                                      | 0.4087                       | 14.4                                  | 16.5                            | 670.223          | 670.200               |
| 707.76                                      | 0.4076                       | 14.4                                  | 16.2                            | 670.213          |                       |
| 707.83                                      | 0.3919                       | 14.5                                  | 15.9                            | 670.166          |                       |
| 707.88                                      | 0.3926                       | 14.4                                  | 16.7                            | 670.228          |                       |
| 707.71                                      | 0.4132                       | 14.4                                  | 17.3                            | 670.194          |                       |
| 707.75                                      | 0.4132                       | 14.4                                  | 17.4                            | 670.232          |                       |
| 707.83                                      | 0.3932                       | 14.5                                  | 15.7                            | 670.182          |                       |
| 707.84                                      | 0.3929                       | 14.4                                  | 15.3                            | 670.190          |                       |
| 707.75                                      | 0.4105                       | 14.5                                  | 16.9                            | 670.218          |                       |
| 707.73                                      | 0.4104                       | 14.4                                  | 16.2                            | 670.199          |                       |
| 707.79                                      | 0.4009                       | 14.5                                  | 18.0                            | 670.192          |                       |
| 707.78                                      | 0.3983                       | 14.6                                  | 17.4                            | 670.161          |                       |

<sup>\*</sup> *Loc. cit.*

*Steam Point*

| Observed pressure in millimetres corrected. | Volume of dead space in c.c. | Temperature centigrade of cloud space. | Temperature centigrade of stem. | Barometric pressure. | Temperature centigrade of stem. | $P_{\theta}$ . | $P_{\theta} - P_0$ (mean). | $P_{\theta} - P_0$ (mean) $\theta$ |
|---------------------------------------------|------------------------------|----------------------------------------|---------------------------------|----------------------|---------------------------------|----------------|----------------------------|------------------------------------|
| 964.52                                      | 0.4004                       | 14.1                                   | 22.7                            | 772.1                | 100.117                         | 917.519        | 217.310                    | 2.46218                            |
| 964.53                                      | 0.4000                       | 14.1                                   | 21.1                            | 772.0                | 100.141                         | 917.508        | 217.348                    | 2.46255                            |
| 964.53                                      | 0.3938                       | 14.5                                   | 22.0                            | 771.5                | 100.425                         | 917.461        | 247.261                    | 2.46215                            |
| 964.54                                      | 0.3950                       | 14.5                                   | 23.2                            | 771.2                | 100.415                         | 917.480        | 247.280                    | 2.46238                            |
| 964.16                                      | 0.4199                       | 14.1                                   | 22.4                            | 770.6                | 100.392                         | 917.437        | 247.237                    | 2.46272                            |
| 964.14                                      | 0.4240                       | 14.5                                   | 23.2                            | 770.8                | 100.400                         | 917.466        | 247.266                    | 2.46281                            |
| 964.36                                      | 0.4064                       | 14.5                                   | 22.5                            | 770.6                | 100.392                         | 917.444        | 247.244                    | 2.46270                            |
| 964.38                                      | 0.4053                       | 14.5                                   | 23.0                            | 770.8                | 100.400                         | 917.453        | 247.253                    | 2.46268                            |
| 964.27                                      | 0.4164                       | 14.5                                   | 22.3                            | 771.1                | 100.410                         | 917.481        | 247.281                    | 2.46274                            |
| 964.28                                      | 0.4119                       | 14.6                                   | 21.7                            | 771.2                | 100.415                         | 917.493        | 247.293                    | 2.46271                            |
| 964.38                                      | 0.3999                       | 14.6                                   | 21.4                            | 770.5                | 100.388                         | 917.405        | 247.205                    | 2.46250                            |
| 964.37                                      | 0.4019                       | 14.5                                   | 20.0                            | 770.5                | 100.388                         | 917.415        | 247.215                    | 2.46260                            |

$$\text{Mean } \frac{P_{\theta} - P_0}{\theta} (\text{mean}) = 2.46258.$$

$$\text{Mean coefficient} = 0.00367440.$$

## Final Results.

| Number of series. | Ice point.                                  |                         |              | Steam point.            |                                      | Coefficient. |
|-------------------|---------------------------------------------|-------------------------|--------------|-------------------------|--------------------------------------|--------------|
|                   | Initial pressure in millimetres of mercury. | Number of observations. | Mean $P_0$ . | Number of observations. | Mean $\frac{P_\theta - P_0}{\theta}$ |              |
| I                 | 698.3                                       | 12                      | 661.248      | 28                      | 2.42848                              | 0.0036726    |
| II                | 378.6                                       | 12                      | 358.444      | 12                      | 1.3154                               | 0.0036697    |
| III               | 707.8                                       | 12                      | 670.200      | 12                      | 2.46253                              | 0.0036744    |
| IV                | 369.1                                       | 10                      | 349.588      | 10                      | 1.2828                               | 0.0036700    |
| V                 | 695.6                                       | 2                       | 658.685      | 2                       | 2.42039                              | 0.0036745    |

Five series of observations were taken, which are indicated in the first column of the table by Roman figures. The pressure of the gas, when the bulb was in ice, is tabulated in the second column. In the third and fifth columns the number of individual observations are recorded. The final corrected values of  $P_0$  and  $\frac{P - P_0}{\theta}$  are inserted in the fourth and sixth columns respectively.

After Series I had been taken, about half of the oxygen contained in the bulb was allowed to escape, and the second series obtained. The thermometer bulb was then completely evacuated and refilled with fresh oxygen, which was used in Series III and IV. The thermometer was again evacuated and refilled with fresh oxygen, with a view to taking another set of observations; but owing to an unfortunate accident to the apparatus, the work was interrupted after the two observations recorded in Series V had been obtained.

On plotting the values of the coefficient against the initial pressures, the value at zero initial pressure is found on linear extrapolation to lie between 0.003664 and 0.003665, a value which is higher than that similarly obtained for nitrogen from Chappuis's determinations, and likewise higher than the pressure coefficient of hydrogen, 0.0036625, obtained by Travers and Jaquerod. The difference, although possibly within the limits of experimental error, might be explained on some such assumption as the association of the gas molecule at lower temperatures.

*Calculation of the Thermodynamical Correction at Zero Temperature from the Pressure Coefficient and known Data.*

It is of interest to deduce the scale correction at 0° C for oxygen, using the method suggested by Callendar,\* and the coefficient calculated above. The notation adopted is as follows:—

\* 'Phil. Mag.,' vol. 25, 1903, p. 48.

$E$  = intrinsic energy of fluid per unit mass.

$p$  = pressure ;  $v$  = volume of unit mass.

$F = E + pv$  = total heat of fluid per unit mass.

$H$  = heat supplied per unit mass from external sources.

$Q = (d\theta/dp)_F$  = "cooling effect" or fall of temperature per unit fall of pressure in adiabothermal expansion at constant  $F$ .

$S = (dH/d\theta)_p$  = specific heat of fluid at constant pressure.

$T = (pv/R)$  = temperature by gas thermometer.

$\theta$  = temperature on thermodynamic scale.

At the point in the neighbourhood of  $50^\circ \text{C.}$ , the degrees on the scale of the gas thermometer are of the same size as those on the absolute scale,  $dT/d\theta = 1$ , and as is shown in the paper quoted above, the difference between the temperature on the gas scale and on the absolute scale is given approximately by the formula

$$\theta - T = Sp \frac{Q}{R} + \left( \frac{d(pr)}{dp} \right)_\theta \frac{p}{R} \dots\dots\dots (1).$$

The term  $(d(pr)/dp)_\theta$  can be evaluated, as shown by Callendar, in the following manner:—Assuming the characteristic equation of the gas to be

$$r = \frac{R\theta}{p} - c + b \dots\dots\dots (2),$$

where

$$c = \frac{a}{R\theta^n} = c_0 \left( \frac{\theta_0}{\theta} \right)^n \dots\dots\dots (3).$$

it may be shown that

$$SQ = (n+1) c - b \dots\dots\dots (4),$$

and that

$$d(pr)/dp = -(c - b) \dots\dots\dots (5).$$

The index  $n$  depends on the nature of the gas, and may be taken as 1.5 for oxygen.

From the Joule-Thomson results,\* we have for oxygen at  $92^\circ \text{C.}$   $SQ = 1.41 \text{ c.c.}$ , and at  $8.7^\circ \text{C.}$ ,  $SQ = 2.88 \text{ c.c.}$  ;  $S$  being expressed in units of  $10^6 \text{ ergs.}$

Hence from equations (3) and (4),

$$c_0 = 1.92 \text{ c.c. and } b = 1.70 \text{ c.c.}$$

At  $50^\circ \text{C.}$ ,

$$c = 1.49,$$

substituting in equation (5)

$$d(pr)/dp \text{ at } 50^\circ \text{C.} = -(1.49 - 1.70) = +0.21 \text{ c.c.}$$

\* Joule's Collected Papers, vol. 2, p. 348.

Taking  $SQ = 1.98$  c.c. at  $50^\circ$  C., which is obtained by interpolating between  $0^\circ$  and  $100^\circ$  C., on the assumption that the cooling effect varies inversely as the square of the absolute temperature, and taking the mean of the results so obtained; taking  $R = 2.59 \times 10^6$ , and  $p$  (the pressure at  $50^\circ$  C.) = 81 cm. mercury =  $1.08 \times 10^6$  (CGS), we have from equation (1)  $\theta - T = 0.913$ . Hence since the scale correction at  $50^\circ$  C. may be neglected in comparison with the zero correction,  $\theta_0 - T_0 = 0.913$ .

Now the pressure coefficient, as determined above, at an initial pressure of 70 cm. of mercury is 0.003674, whence

$$T_0 = \frac{1}{0.003674} = 272^\circ.18.$$

$\theta_0$  is thus equal to  $273.09$ , a result which is in good agreement with the value of the same quantity obtained by Callendar\* for air, nitrogen, and hydrogen.

It will be observed by reference to equation (5) that  $d(pv)/dp$  changes sign at a temperature  $23^\circ$  C., at the pressure employed in the above experiments.

In conclusion we desire to express our very best thanks to Dr. Travers, not only for his kindness in putting his apparatus at our disposal, but also for the unfailing interest which he has shown in the progress of the work.

\* *Loc. cit.*

"The Vapour Pressures of Liquid Oxygen on the Scale of the Constant-volume Oxygen Thermometer filled at different Initial Pressures." By MORRIS W. TRAVERS, D.Sc., Fellow of University College, London, and CHARLES J. FOX, B.Sc., Ph.D. Communicated by Sir WILLIAM RAMSAY, K.C.B., F.R.S. Received June 26, 1903.

The vapour pressures of liquid oxygen and liquid hydrogen on the scales of the constant-volume hydrogen and helium thermometers has recently been determined by one of us in conjunction with Dr. A. Jaquerod and Mr. G. Senter, and it has been found that two scales of temperature differ by amounts which increase as the temperature falls.

|                       | Vapour<br>pressure. | Hydrogen<br>scale. | Helium<br>scale. |
|-----------------------|---------------------|--------------------|------------------|
| Liquid oxygen .....   | 760 mm.             | 90°·10             | 90°·20           |
| Liquid hydrogen ..... | 760                 | 20°·22             | 20°·41           |

These results are in accordance with Callendar's calculations of the deviation from the thermo-dynamic scale of measurements with thermometers filled at an initial pressure of 1000 mm. of mercury at the melting point of ice. Whether the deviation becomes smaller when the thermometers are filled at a lower pressure has not been determined, and, indeed, with the means at our disposal it would be practically impossible to do so. In order, therefore, to investigate the variation of the readings of the gas thermometer with change of initial pressure, we decided to measure the vapour pressures of liquid oxygen on the scales of the constant-volume oxygen and nitrogen thermometers, for which the deviations from the thermo-dynamic scale are considerably greater.

*Previous investigations.*—The vapour pressure of liquid oxygen has been determined by Dewar,\* at temperatures near the boiling point, by means of a constant-volume oxygen thermometer. In calculating his results he employed the value 0·0036525 for the pressure coefficient of oxygen.

*The pressure coefficient of oxygen.*—Makower and Noble,† using the apparatus and method of Travers and Jaquerod, have determined the pressure coefficient of oxygen at pressures corresponding to 375 and 700 mm. of mercury. Their results lead to the conclusion that the coefficient increases with rise of pressure, and if the variation can be

\* 'Roy. Soc. Proc.,' 1901, vol. 68, p. 44.

† 'Roy. Soc. Proc.,' p. 379 ante.

assumed to be a linear function of the initial pressure  $P_0$ , it may be expressed by the formula

$$\alpha = 0.0036642 + 0.00000001457P_0,$$

where  $P_0$  is expressed in millimetres.

In the equation employed to calculate the temperature on the gas scale,\* the reciprocal of the coefficient corresponding to the pressure  $P_0$  replaces the corresponding values, 273.03 (or 273), for the ice point on the helium or hydrogen scales.

*Apparatus and method of experiment.*—The apparatus employed in these experiments was identical with that described by Travers, Senter, and Jaquero,† and employed by them in measuring the vapour pressure of liquid oxygen and liquid hydrogen on the constant volume hydrogen and helium scales. The volumes of the different parts of the apparatus were as follows:—

|                                  |             |
|----------------------------------|-------------|
| Volume of the bulb at 0° C. .... | 24.264 c.c. |
| Volume of the stem.....          | 0.0625      |
| Volume of the dead space .....   | 0.473       |

The method of experiment has already been fully described.‡

As the thermometer was a new one, it was thought advisable to fill it first of all with hydrogen, and to measure the vapour pressures of liquid oxygen on the hydrogen scale. The results, which were perfectly satisfactory, are as follows:—

#### Ice Point.

|                               |           |
|-------------------------------|-----------|
| Pressure on gas .....         | 959.6 mm. |
| Temperature of dead space ... | 16° 8 C.  |
| Constant .....                | 86.863    |

The constant is the product of the pressure on the gas at the melting point of ice and the volume which the whole of the gas in the thermometer would occupy at that temperature, divided by the value of the temperature of the melting ice on the gas scale. The latter is the reciprocal of the pressure-coefficient for the gas corresponding to that particular pressure. Since the constant involves the three terms  $p$ ,  $v$ , and  $T$ , in the simple gas equation, a knowledge of it enables us to calculate temperatures, on the same scale, from observed pressures, when the volume is constant.

\* 'Phil. Trans.,' A, vol. 200, p. 145.

† 'Phil. Trans.,' A. vol. 200, p. 141.

‡ *Loc. cit.*



### Vapour Pressures of Liquid Oxygen on the Hydrogen Scale.

|                                      |            |            |
|--------------------------------------|------------|------------|
| Pressure on gas in thermometer ..... | 286.55 mm. | 286.65 mm. |
| Temperature of dead space .....      | 16°·5 C.   | 16°·6 C.   |
| Temperature of stem .....            | 126°·0     | 126°·0     |
| Vapour pressure of oxygen .....      | 235.4 mm.  | 236.5 mm.  |
| Temperature—                         |            |            |
| On new thermometer .....             | 80°·27     | 80°·30     |
| From previous measurements .....     | 80°·26     | 80°·29     |

*Preparation of the oxygen.*—The oxygen employed was obtained by heating pure potassium permanganate contained in a glass tube, connected with the thermometer through a tube containing soda lime and a glass spiral, which could be immersed in liquid air; all the junctions were made by sealing together the various glass tubes in the blowpipe flame. The thermometer was first exhausted; oxygen was generated from the potassium permanganate, and allowed to liquefy in the glass spiral, and then to enter the thermometer. The latter was thoroughly washed out with the gas before it was finally filled.

### Vapour Pressures of Liquid Oxygen on the Constant-volume Oxygen Scale.

I.—Ice Point. December 10, 1902.

|                              |            |
|------------------------------|------------|
| Pressure on gas .....        | 658.55 mm. |
| Temperature of dead space .. | 15°·2 C.   |
| Pressure coefficient .....   | 0.0036738  |
| Constant .....               | 59.993     |

### Vapour Pressures of Liquid Oxygen.

December 12.

|                                  |           |           |           |
|----------------------------------|-----------|-----------|-----------|
| Pressure on gas in thermometer   | 203.7 mm. | 204.6 mm. | 205.3 mm. |
| Temperature of dead space .....  | 15°·9 C.  | 15°·7 C.  | 15°·2 C.  |
| Temperature of stem .....        | 115°·5    | 124°·0    | 130°·0    |
| Vapour pressure of oxygen .....  | 369.9 mm. | 382.9 mm. | 394.8 mm. |
| Temperature on oxygen scale ...  | 82°·62    | 83°·10    | 83°·37    |
| Deviation from helium scale .... | 1°·21     | 1°·02     | 1°·01     |

December 15.

|                                 |           |           |           |
|---------------------------------|-----------|-----------|-----------|
| Pressure on gas in thermometer  | 208.8 mm. | 209.3 mm. | 209.7 mm. |
| Temperature of dead space ..... | 17°·4 C.  | 17°·3 C.  | 17°·5 C.  |
| Temperature of stem .....       | 110°·0    | 112°·0    | 113°·0    |
| Vapour pressure of oxygen ..... | 477.8 mm. | 488.1 mm. | 498.2 mm. |
| Temperature on oxygen scale...  | 84°·88    | 85°·04    | 85°·15    |
| Deviation from helium scale ... | 1°·10     | 1°·14     | 1°·19     |

## II.—Ice Point. December 22, 1902.

|                               |           |
|-------------------------------|-----------|
| Pressure on gas .....         | 483·8 mm. |
| Temperature of dead space ... | 17°·9 C.  |
| Pressure coefficient .....    | 0·0036713 |
| Constant .....                | 43·993    |

## Vapour Pressures of Liquid Oxygen.

December 22.

|                                     |            |            |
|-------------------------------------|------------|------------|
| Pressure on gas in thermometer..... | 147·55 mm. | 147·60 mm. |
| Temperature of dead space .....     | 18°·7 C.   | 18°·9 C.   |
| Temperature of stem .....           | 125°·0     | 125°·0     |
| Vapour pressure of oxygen .....     | 300·0 mm.  | 301·5 mm   |
| Temperature on oxygen scale .....   | 81°·47     | 81°·47     |
| Deviation from helium scale .....   | 0°·62      | 0°·72      |

December 29.

|                                      |            |            |            |            |
|--------------------------------------|------------|------------|------------|------------|
| Pressure on gas in thermometer ..... | 146·12 mm. | 146·52 mm. | 147·22 mm. | 148·42 mm. |
| Temperature of dead space .....      | 15°·4 C.   | 15°·4 C.   | 15°·9 C.   | 16°·1 C.   |
| Temperature of stem .....            | 104°·0     | 104°·0     | 115°·0     | 130°·0     |
| Vapour pressure of oxygen .....      | 283·6 mm.  | 291·4 mm.  | 297·1 mm.  | 332·2 mm.  |
| Temperature on oxygen scale.....     | 80°·74     | 80°·95     | 81°·34     | 82°·00     |
| Deviation from helium scale .....    | 1°·00      | 0°·99      | 0°·77      | 0°·99      |

## III.—Ice Point. January 2, 1903.

|                              |           |
|------------------------------|-----------|
| Pressure on gas .....        | 731 mm.   |
| Temperature of dead space... | 18°·1 C.  |
| Pressure coefficient .....   | 0·0036748 |
| Constant .....               | 66·524    |

## Vapour Pressures of Liquid Oxygen.

January 2, 1903.

|                                 |            |           |           |
|---------------------------------|------------|-----------|-----------|
| Pressure on gas in thermometer  | 218·65 mm. | 218·8 mm. | 219·0 mm. |
| Temperature of dead space ..... | 18°·9 C.   | 18°·4 C.  | 18°·3 C.  |
| Temperature of stem .....       | 92°·5      | 92°·5     | 92°·5     |
| Vapour pressure of oxygen ..... | 260·0 mm.  | 262·5 mm. | 265·0 mm. |
| Temperature on oxygen scale ... | 79°·90     | 78°·96    | 80°·4     |
| Deviation from helium scale ... | 1°·18      | 1°·18     | 1°·18     |

## IV.—Ice Point. January 2, 1903.

|                                 |           |
|---------------------------------|-----------|
| Pressure on gas .....           | 336.0 mm. |
| Temperature of dead space ..... | 17°·0 C.  |
| Pressure coefficient .....      | 0.0036692 |
| Constant .....                  | 30.538    |

## Vapour Pressures of Liquid Oxygen.

|                                      |           |           |           |            |
|--------------------------------------|-----------|-----------|-----------|------------|
| Pressure on gas in thermometer ..... | 109.3 mm. | 109.4 mm. | 109.7 mm. | 109.85 mm. |
| Temperature of dead space .....      | 16°·8 C.  | 16°·7 C.  | 16.7 C.   | 16.7 C.    |
| Temperature of stem .....            | 116°·0    | 116°·0    | 121°·0    | 121°·0     |
| Vapour pressure of oxygen .....      | 591.8 mm. | 591.8 mm. | 614.1 mm. | 618.5 mm.  |
| Temperature on oxygen scale.....     | 87°·04    | 87°·14    | 87°·40    | 87°·50     |
| Deviation from helium scale .....    | 0°·82     | 0°·72     | 0°·78     | 0°·78      |

*Discussion of the results.*—The mean values of the difference of the temperatures corresponding to the vapour pressure of liquid oxygen on the scales of the oxygen and helium thermometers, when plotted against the initial pressures at which the oxygen thermometer was filled, are found to lie nearly on a straight line. The smoothed results are as follows:—

| Initial pressure. | $\Delta$ found. | $\Delta$ smoothed. |
|-------------------|-----------------|--------------------|
| 1000 mm.          | —               | 1.5                |
| 731               | 1.18            | 1.18               |
| 658               | 1.11            | 1.11               |
| 484               | 0.85            | 0.89               |
| 336               | 0.77            | 0.72               |
| 0                 | —               | 0.4                |

The values at 1000 mm. and at zero pressure are obtained by extrapolation.

According to Callendar,\* the deviations of the constant volume helium and hydrogen thermometers from the thermo-dynamic scale should, at low temperatures, be equal and opposite in sign. According to this, the deviation of the boiling point of oxygen measured on the scale of an oxygen thermometer, filled at an initial pressure of 1000 mm., is 1.4 below the true temperature, while the deviation in the case of the boiling point of hydrogen on the scale of a hydrogen thermometer is 0.1, the thermometers being filled at an initial pressure of 1000 mm.

\* Loc. cit.

The deviation in the case of the hydrogen thermometer at the boiling point of that gas, supposing Callendar's results to be correct, appears relatively small, though the discrepancy is really due to the method of expressing the results, a degree at the lower temperature having a greater thermo-dynamic significance than at the higher temperature.

The fact that the value of the deviation does not vanish at zero pressure may possibly be due to a tendency of the gaseous molecules to associate. This tendency would be less affected by change of pressure than by change of temperature.\*

"On an Approximate Solution for the Bending of a Beam of Rectangular Cross-section under any System of Load.—Additional Note." By L. N. G. FILON, M.A., D.Sc. Communicated by Dr. C. CHREE, F.R.S. Received September 12, 1903.

My attention has lately been called by M. Flamant to certain discrepancies in some formulæ given by me in a paper recently published under the above title.†

On investigation I have found that a set of formulæ of the paper in question, namely, those of § 41, contained several inaccuracies.

I am unable to account for the introduction of these errors into the paper, and can only express my great regret that this mistake occurred and that I failed to detect it in time to remedy it before the paper was finally printed.

The most important of the final results, those relating to the stresses are, fortunately, correctly given.

The object of this short note is to give the results of § 41 of the paper referred to, in their amended form.

Equation (111) should read

$$\frac{B_1}{4} + D_1 + b^2 \left( -\frac{15B_3}{4} - 3D_3 \right) = 0$$

The equations following are correct, until we come to (128), which should be

$$B_3 = \frac{1}{3b^2} \left( D_1 + \frac{B_1}{4} \right),$$

$$D_3 = -\frac{1}{12b^2} \left( D_1 + \frac{B_1}{4} \right).$$

\* Ramsay, 'Phys. Soc. Proc.'

† 'Phil. Trans.,' A, vol. 201, pp. 63—155.

The values of U, V, P, at the bottom of p. 149, should read

$$U = \text{const.} + x \left\{ A_1 \frac{\lambda' + 3\mu}{8\mu(\lambda' + \mu)} + \frac{C_1}{2\mu} \right\} + \frac{B_1 y}{E} + \frac{B_2}{E} 2xy \\ - \frac{3}{8\mu} \frac{qxy}{b} + \left( \frac{B_1}{4} + D_1 \right) \left\{ \frac{y}{2\mu} + \frac{1}{b^2} \left[ \frac{x^2 y}{E} - \frac{y^3}{3} \left( \frac{1}{E} + \frac{1}{2\mu} \right) \right] \right\} \\ - \frac{q}{4b^3} \left\{ \frac{x^2 y}{E} - xy^3 \left( \frac{1}{E} + \frac{1}{2\mu} \right) \right\}.$$

$$V = \text{const.} - y \left\{ A_1 \frac{\lambda' - \mu}{8\mu(\lambda' + \mu)} + \frac{C_1}{2\mu} \right\} - \frac{B_1 x}{E} - \frac{B_2}{E} (x^2 - \eta y^2) \\ - \frac{3q}{16\mu b} \frac{(x^2 - y^2)}{b} + \left( \frac{B_1}{4} + D_1 \right) \left\{ \frac{x}{2\mu} - \frac{1}{b^2} \left( \frac{x^3}{3E} - \eta \frac{xy^3}{E} \right) \right\} \\ + \frac{q}{16b^3} \left\{ \frac{x^4}{E} - \eta \frac{6x^2 y^2}{E} + y^4 \left( \frac{1}{E} - \frac{1}{\mu} \right) \right\}.$$

$$P = \left( \frac{3A_1}{4} + C_1 \right) + 2B_2 y - \frac{3qy}{4b} + \frac{2xy}{b^2} \left( \frac{B_1}{4} + D_1 \right) \\ - \frac{3}{4} \frac{x^2 y q}{b^3} + \frac{qy^3}{2b^3}.$$

The values of Q and S at the bottom of p. 149 are correct.

The value of  $B_2$  on p. 150 should be

$$B_2 = \frac{3}{8} \frac{qa^2}{b^3} + \left( \frac{9}{40} \right) \frac{q}{b}.$$

The values of P, Q, S on p. 150 are correct.

The values of U and V, on the same page, ought to be

$$U = \frac{\eta x q}{2E} + \frac{3}{4} \frac{qa^2 xy}{Eb^3} + \left( \frac{9}{20} \right) \frac{qxy}{Eb} - \frac{3}{8} \frac{qxy}{\mu b} - \frac{q}{4b^3} \left\{ \frac{x^2 y}{E} - xy^3 \left( \frac{1}{E} + \frac{1}{2\mu} \right) \right\}.$$

$$V = \frac{yq}{2E} - \left( \frac{3}{8} \frac{a^2}{b^3} + \frac{9}{40b} \right) \frac{q}{E} (x^2 - \eta y^2) - \frac{3}{16} \frac{q(x^2 - y^2)}{\mu b} \\ + \frac{q}{16b^3} \left\{ \frac{x^4}{E} - \eta \frac{6x^2 y^2}{E} + y^4 \left( \frac{1}{E} - \frac{1}{\mu} \right) \right\}.$$

In § 42 the value of  $(d^2 V/dx^2)_{y=0}$ , which was derived from the erroneous V of page 150, should be

$$- \frac{3}{4} \frac{(a^2 - x^2)}{Eb^3} q - \frac{q}{Eb} \left\{ \frac{6}{5} - \frac{3\eta}{4} \right\}.$$

Since  $\eta$  is negative (with zero for an extreme value), the last result

shows that the constant term in the curvature is, in general, increased numerically by the correction. Further, this constant term involves the *two* elastic constants.

The general conclusions drawn with regard to the beam under a uniform load are in no way affected.

“On the Sensation of Light produced by Radium Rays and its Relation to the Visual Purple.” By W. B. HARDY, F.R.S., Caius College, Cambridge, and H. K. ANDERSON, M.D., Caius College, Cambridge. Received September 20, 1903.

It is now well known that when a few milligrammes of a salt of radium are brought near the head in the dark a sensation of diffuse light is produced. We have examined this phenomenon with the object (1) of determining the place of origin of the sensation ; (2) of identifying the particular rays which cause it.

The rays from radium falling upon the skin produce no sensation, and we failed in evoking sensations of sound, smell, or taste by their agency. The only response immediately traceable to them seems to be this one of diffuse luminosity.

It may be described as an appearance of diffuse light of steady intensity disposed in the external space in front of the head and filling that space fairly or quite uniformly. If the radium, covered of course with some opaque screen such as, for instance, black cardboard, to cut off the pale light which it emits, be held in front of one eye, one notices that the intensity of the glow is considerably reduced by closing the eyelid. When the eye is open it is possible in a very general way to locate the radium from the fact that the sensation is strongest when the axis of vision is directed to it and diminishes when the head is turned to one side. The sense of direction arises solely from variations in the intensity of the glow and not from variations in its quality.

When the eye is closed the sense of locality is completely lost. This is due to the fact, to be dealt with more fully presently, that the glow is due to the  $\beta$  and  $\gamma$  rays, and that the eyelid is peculiarly opaque to the former, stopping apparently the whole of them. The  $\gamma$  rays, on the other hand, having a very great penetrating power, pass almost equally well through the eyelid or through the bones and other tissues forming the orbit. There is, therefore, no possibility of a differential screening action when once the eyelids are closed and the  $\beta$  rays stopped, with the result that all sense of the direction of the source of light is lost.

The sensation of light is purely of retinal origin. It is not due to

a response to the rays on the part of the optic nerve, the optic tract, or the brain itself. We were led to this conclusion in the following way. When the crystals of radium bromide are spread out so as to form a layer about 1 mm. deep, covering a circle of about 5 mm. diameter, the glow is very intense when the flat face of the layer is presented to the eye,\* and practically vanishes when the layer is turned edgewise. This must be due to the fact that the volume of the stream of rays is roughly proportional to the surface of the mass of the salt, and that the stream is densest in a plane normal to the surface. The effect of rapidly rotating the little plate of crystals before the eye is very striking; it is as though a series of blinding flashes of light were thrown on to the retina.

If now the radium be moved about over the surface of the head, one notices that for the sensation of light to be present the axis of greatest ray density must cut one or other eyeball, and that the further the radium is removed from an eyeball the weaker is the sensation.

This statement can be illustrated by the following case. When the radium is held with the face of the crystals opposite the middle of the forehead, there is at most a luminosity so feeble as to be detected with difficulty; at the same time no other sensations are evoked. If, however, the plate of crystals be rotated downwards and outwards so as to face towards one eyeball, a strong light is at once seen with that eye.

Experimenting in this way, we convinced ourselves that no sensations are directly produced by the rays reaching the brain substance,† and that the origin of the sensation of light lies solely in the eyes themselves.

On passing directly from daylight into a dark room one's eyes are at first almost completely insensitive to the rays, and sensitiveness grows only slowly. In the evening, after exposure for some hours to yellow artificial light, the sensation of light is felt almost immediately the ordinary sources of light are extinguished. Radium vision, if we may so call it, will continue to increase for a full hour in the dark—in other words, it is a phenomenon of the dark-adapted eye.

Radium vision, therefore, resembles the response to light of low intensity, and as a great many facts go to show that this is connected with the visual purple, we examined the effect of the rays upon that substance. To our surprise we were unable to detect any

\* To avoid repetition, it must be understood that the crystals are always covered with opaque paper or cardboard, so as to exclude the actual light rays.

† This statement is of course limited to the stream of rays from 50 milligrammes of radium bromide. It is possible that a more powerful stream might evoke direct response from the brain.

bleaching action whatever on the visual purple of the eye of the frog or rabbit.

The method we adopted was to keep the animal in the dark for some hours, to kill it and dissect out the retinae in sodium light, and to expose one retina to the rays from 50 milligrammes of pure radium bromide in a moist dark chamber, while the other retina remained in a similar dark chamber as a control.

The retinae, when removed, were spread on to thin sheets of mica and placed over the radium at about 3 mm. distance, in such a way that either the mica alone was between the radium and the retina, or the mica and a layer of opaque black paper to screen off the light rays. In a few cases the retina was so placed that nothing more than about 2 mm. of air separated it from the radium. The time of exposure was, as a rule, 20 hours. In no case was there any difference in tint between the exposed and the unexposed retinae, while both control and exposed retinae were found to bleach in full daylight in a few seconds.

It will be noticed that in those experiments in which the light rays from the radium were allowed to fall on the retina, no bleaching could be detected. This does not prove that they were wholly without action since, as Kühne showed, even the excised retina has a feeble power of reproducing the purple. The experiments prove merely that the  $\alpha$ ,  $\beta$ , and  $\gamma$  rays, either alone or with the light rays, fail to overcome this recuperative power sufficiently to effect a detectable decrease in the quantity of pigment in 20 hours.

When one considers the density and activity of the stream of "invisible" rays at 3 mm. distance from 50 mm. of radium bromide, we may fairly conclude that these rays have no action on the pigment. This conclusion led us to consider whether the sensation of light which is caused by the invisible rays, is, indeed, due to the direct response of the retina. When one considers how limited in extent is that portion of the spectrum to which the retina responds, it would be a matter of surprise if so specialised an instrument were found to respond to rays as different from light-waves as are the radium rays. The evidence we have been able to obtain points to the conclusion that the retina probably does not respond directly to the radium rays, but to light rays, which are given out by the tissues of the eyeball—chiefly the cornea and lens—when they are traversed by the  $\beta$  and  $\gamma$  rays.

The fresh lens of a sheep, ox, or rabbit was found to glow strongly when exposed to the rays. The cornea and vitreous humour also glow, but to a less extent, and the retina itself gives a strong glow. The sclerotic, on the other hand, glows very slightly. The glow of the lens alone is so striking as fully to account for the sensation of light produced by the rays.



This quality of emitting light under the influence of the rays is not at all peculiar to the tissues of the eyeball. The skin glows, as may readily be seen by bringing the hand near to radium covered by opaque paper. Fat and muscle glow strongly.

The fact that direct stimulation of the retina contributes at most but little to the sensation of light, comes out clearly when the nature of the rays which cause the sensation and their power of penetrating the eyeball are examined. From this investigation the  $\alpha$  rays were always excluded. They possess so little penetrating power that they are arrested by the thickness of opaque paper which is necessary in order to screen off the light rays.

The  $\beta$  and  $\gamma$  rays, therefore, remain for consideration, and they both contribute to the production of the sensation of light.

The following experiment proves this:—

Fifty milligrammes of radium bromide, covered with opaque paper, were placed at the bottom of a thick-walled lead tube 6 cm. in length, on each side of which were the poles of an electric magnet giving a field of more than 5000 lines over nearly the entire length of the lead tube. The physical effect of this field would be to divert the  $\beta$  rays into the lead. The optical effect was very striking. When the field was established while the eye was applied to the tube, the glow suddenly diminished to what appeared to be about a-fifth or less of its previous intensity. The change resembles the sudden turning down of a gas light. The persistent or residual glow must be that due to the  $\gamma$  rays.

The effect of the  $\gamma$  rays can be demonstrated by screening off the  $\beta$  rays with lead screens. A plate of lead 2.3 mm. thick was found to reduce the intensity of the glow very much. Such a plate cuts off the  $\beta$  rays. The further addition of four more such screens, thus increasing the thickness of the lead to 11.5 mm., scarcely diminishes the remaining glow, for they arrest only a small fraction of the  $\gamma$  rays. In these screen experiments it is, of course, necessary to keep the distance between the radium and the eye constant. This was effected by a simple apparatus designed for the purpose which does not need description.

The glow is still quite strong when 4 cm. of lead are interposed between the eye and the radium (50 milligrammes), but it is faint with more than 5 cm.

Similarly the fluorescence of the excised lens of the eye which is excited by those rays which traverse lead 2.3 mm. in thickness is not sensibly diminished by adding two more such screens, thereby increasing the thickness to 6.9 mm.

So far as the  $\beta$  rays are concerned, it is certain that they cause a sensation of light solely by inducing fluorescence of the tissues of the eyeball in front of the retina. Taking the eyeball of the sheep as corre-

sponding in size fairly well with the human eyeball, it was found by measurement with the electroscope that the cornea, lens, and front half of the vitreous humour taken together had the same screening action as 6.6 mm. of lead. That is to say, they arrested all the  $\beta$  rays and a measurable fraction of the  $\gamma$  rays. Therefore the  $\beta$  rays do not penetrate to the retina, except perhaps in small quantity to the most anterior portion.

The part played by the  $\gamma$  rays is not so obvious. It is certain that they can excite the excised lens to become luminous, since a lens separated from the radium by a centimetre of lead emits light enough to be visible. The fluorescence is, however, exceedingly faint, much less for instance than that excited in a piece of glass of about the same size. On the other hand, the sensation of light evoked by those rays which traverse even 4 cm. of lead is quite considerable, and no one can fail to be struck with the fact that the fluorescence of an excised lens and the sensation of light produced by the  $\gamma$  rays are very dissimilar values. It is, therefore, possible that the  $\gamma$  rays produce the sensation of light in part only when they actually strike the retina. Here again, however, the response need not be directly to the  $\gamma$  rays but to light-waves started in the retina itself, for, as has been already pointed out, the excised retina glows strongly when brought near radium.

The following experiment helps to prove that the  $\gamma$  rays produce the sensation of light in great part when they actually strike the retina. The radium was covered with 5 mm. of lead to cut off the  $\beta$  rays, and a vertical plate of lead 40 mm. deep and 2 mm. thick was moved backwards and forwards over the radium so as to form a bar-like screen 40 mm. thick and 2 mm. wide between it and the eye. The effect produced was that of a bar of shadow moving across the glow.

Now the  $\gamma$  rays are not refrangible, and therefore the vertical lead screen would cast a partial shadow its own breadth upon the lens and retina. The effect upon the lens would be to diminish its fluorescence, but as the light-waves are given off in all directions from the lens, there would not be a definite shadow on the retina. Therefore this bar-like shadow must be due to the shadow on the retina itself.

Reference was made in passing to the remarkable stopping power of the eyelid. The human eyelid seems to be capable of arresting all the  $\beta$  rays. With the eyelid closed the insertion of a lead screen 9.2 mm. thick makes no\* difference in the intensity of the sensation of light. This, however, is true only when the eyelids are tightly closed. If they are stretched by raising the eyebrows, and their thickness thereby reduced, the interposition of the lead screen produces a detectable decrease.

\* Many trials with six different individuals resulted in a strong balance of opinion in favour of the screen producing no diminution. Only one person thought he could detect a lessening of the glow.

Some measurements of the screening power of various tissues were made with a Curie electroscope. The numbers give the rate of leak in divisions of the scale per second. The tissues were from a freshly killed rabbit. 5 milligrammes of radium bromide were used, enclosed in a lead capsule having an aperture 4 mm. in diameter on one side.

|                                         |      |
|-----------------------------------------|------|
| Lead, 0.2 mm. thick .....               | 25.0 |
| "    0.4    "    .....                  | 18.0 |
| "    2.3    "    .....                  | 11.3 |
| Skin of back, 0.8 mm. thick .....       | 20.5 |
| "    (shaved), 0.8 mm. thick ...        | 22.0 |
| Eyelid, 0.7 mm. thick.....              | 17.2 |
| Nictitating membrane, 0.8 mm. thick ... | 28.6 |
| Iris .....                              | 28.6 |
| Lens, 7.5 mm. thick .....               | 14.0 |
| Sclerotic } .....                       | 23.0 |
| Choroid } .....                         |      |
| Retina } .....                          |      |
| Sclerotic < 0.5 mm. thick .....         | 36.3 |
| Entire eyeball .....                    | 11.5 |
| Muscle (skeletal), 3.0 mm. thick .....  | 19.0 |

These figures show a remarkable difference in stopping power between the eyelid and the nictitating membrane, in favour of the former, which equals 0.4 mm. of lead. The screening power of the eyelid is also noticeably greater than that of the skin of the back, although the latter is the thicker.

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“The Maximum Order of an Irreducible Covariant of a System of Binary Forms.” By A. YOUNG, M.A., Clare College, Cambridge. Communicated by Major P. A. MACMAHON, D.Sc., F.R.S. Received September 26, 1903.

It has been suggested to me that an incidental result of a paper I have recently communicated to the London Mathematical Society may be of interest. In the paper in question it is proved that all covariants of a system of binary  $n$ -ics are linearly expressible in terms of—

(i) Covariants of the form

$$(a_1 a_2)^{\lambda_1} (a_2 a_3)^{\lambda_2} \dots (a_{s-1} a_s)^{\lambda_{s-1}} a_1^{n-\lambda_1} a_2^{n-\lambda_1-\lambda_2} \dots a_s^{n-\lambda_{s-1}},$$

where

$$\lambda_1 \leq 2^{s-2}, \quad \lambda_2 \leq 2^{s-3}, \quad \dots \quad \lambda_{s-1} \leq 1$$

(ii) Covariants having a symbolical factor

$$(ab)^\lambda (bc)^{n-\lambda} (ca)^\rho$$

(iii) Products of covariants.

Mr. J. H. Grace, in a note appended to the paper, has deduced from this result a means of calculating the maximum order, in the variables, of an irreducible covariant of a system of quantics. If no quantic of the system is of order exceeding  $n$ , the maximum order of an irreducible covariant is the greatest of the numbers

$$n\delta - 2^\delta + 2,$$

where  $\delta$  is an integer,—in fact, the degree in the coefficients of the covariant in question.

If  $n = 2^i + k$  where  $k \geq 2^i$ , it will be seen that the maximum is

$$(i+1)(2^i + k) - 2^{i+1} + 2.$$

The covariant of maximum order is then

$$(a_1 a_2)^{2^{i-1}} (a_2 a_3)^{2^{i-2}} \dots (a_{i-1} a_i)^2 (a_i a_{i+1}) a_1^{n-2^{i-1}} \dots a_{i+1}^{n-1}.$$

There are strong reasons for believing this covariant to be actually irreducible; in the contrary case a reduction is obtained for certain forms classed as perpetuants.\*

\* MacMahon, ‘Camb. Phil. Trans.’ vol. 19, p. 234; Grace, ‘Lond. Math. Soc. Proc.’ vol. 35, p. 107.

The following is a table giving the maximum order for all values of  $n$  from 1 to 100, together with the degree,  $\delta$ , of the covariant of maximum order:—

| $n$ . | Max.<br>order. | $\delta$ . | $n$ . | Max.<br>order. | $\delta$ . | $n$ . | Max.<br>order. | $\delta$ . | $n$ . | Max.<br>order. | $\delta$ . | $n$ . | Max.<br>order. | $\delta$ . |
|-------|----------------|------------|-------|----------------|------------|-------|----------------|------------|-------|----------------|------------|-------|----------------|------------|
| 1     | 1              | 1          | 21    | 75             | 5          | 41    | 184            | 6          | 61    | 304            | 6          | 81    | 441            | 7          |
| 2     | 2              | 1, 2       | 22    | 81             | 5          | 42    | 190            | 6          | 62    | 310            | 6          | 82    | 448            | 7          |
| 3     | 4              | 2          | 23    | 86             | 5          | 43    | 196            | 6          | 63    | 316            | 6          | 83    | 455            | 7          |
| 4     | 6              | 2, 3       | 24    | 90             | 5          | 44    | 202            | 6          | 64    | 322            | 6, 7       | 84    | 462            | 7          |
| 5     | 9              | 3          | 25    | 95             | 5          | 45    | 208            | 6          | 65    | 329            | 7          | 85    | 469            | 7          |
| 6     | 12             | 3          | 26    | 100            | 5          | 46    | 214            | 6          | 66    | 336            | 7          | 86    | 476            | 7          |
| 7     | 15             | 3          | 27    | 105            | 5          | 47    | 220            | 6          | 67    | 343            | 7          | 87    | 483            | 7          |
| 8     | 18             | 3, 4       | 28    | 110            | 5          | 48    | 226            | 6          | 68    | 350            | 7          | 88    | 490            | 7          |
| 9     | 22             | 4          | 29    | 115            | 5          | 49    | 232            | 6          | 69    | 357            | 7          | 89    | 497            | 7          |
| 10    | 26             | 4          | 30    | 120            | 5          | 50    | 238            | 6          | 70    | 364            | 7          | 90    | 504            | 7          |
| 11    | 30             | 4          | 31    | 125            | 5          | 51    | 244            | 6          | 71    | 371            | 7          | 91    | 511            | 7          |
| 12    | 34             | 4          | 32    | 130            | 5, 6       | 52    | 250            | 6          | 72    | 378            | 7          | 92    | 518            | 7          |
| 13    | 38             | 4          | 33    | 136            | 6          | 53    | 256            | 6          | 73    | 385            | 7          | 93    | 525            | 7          |
| 14    | 42             | 4          | 34    | 142            | 6          | 54    | 262            | 6          | 74    | 392            | 7          | 94    | 532            | 7          |
| 15    | 46             | 4          | 35    | 148            | 6          | 55    | 268            | 6          | 75    | 399            | 7          | 95    | 539            | 7          |
| 16    | 50             | 4, 5       | 36    | 154            | 6          | 56    | 274            | 6          | 76    | 406            | 7          | 96    | 546            | 7          |
| 17    | 55             | 5          | 37    | 160            | 6          | 57    | 280            | 6          | 77    | 413            | 7          | 97    | 553            | 7          |
| 18    | 60             | 5          | 38    | 166            | 6          | 58    | 286            | 6          | 78    | 420            | 7          | 98    | 560            | 7          |
| 19    | 65             | 5          | 39    | 172            | 6          | 59    | 292            | 6          | 79    | 427            | 7          | 99    | 567            | 7          |
| 20    | 70             | 5          | 40    | 178            | 6          | 60    | 298            | 6          | 80    | 434            | 7          | 100   | 574            | 7          |

"The Cell Structure of the Cyanophyceæ.—Preliminary Paper."

By HAROLD WAGER. Communicated by D. H. SCOTT, M.A.,  
Ph.D., F.R.S. Received October 9, 1903.

The Cyanophyceæ form a group of plants which resemble the Algae in some respects, but are sharply differentiated from them as regards the structure of their cell contents. During the last 20 years they have been the subject of numerous memoirs in which the problem of their cell structure has been attacked, but with very varying results, and much controversy has arisen concerning the exact nature of the central body or nucleus and the presence or absence of a chromatophore. On the one side, we have observers who deny the existence of a nucleus or chromatophore in these forms, on the other, those who consider that the central body is either a true nucleus or the representative of one, and that the colouring matter is contained in a definite chromatophore.

The investigation of the cytology of these organisms is certainly not an easy one, and it is not astonishing that so many different interpretations are given of the facts observed. But it seems to me that it is not an impossible task to arrive at more definite conclusions than has hitherto been done, although we need to know far more of the cytology of the lower organisms, both plant and animal, before we can determine with any certainty the exact nature of their cell structures or their relationship to other groups.

In attacking the problem it is necessary that the methods used should be as refined as apparatus and re-agents will allow, and it is especially important not only that the highest possible powers of the microscope should be used, but that the illumination should be as perfect as possible. For this purpose a good sub-stage condenser is necessary, and for the finer details of structure an oil immersion condenser has often been used. It is necessary also, in order to obtain good comparable results, that the species investigated should be in a sound and healthy state of development. The cells very soon become altered in character if kept under unfavourable conditions, and many of the contradictory accounts which have been given are probably due, in part, to want of care in this respect.

As regards the preservation and staining of these plants, the ordinary methods used in connection with cytological investigations are sufficient, but special care is required in their application, especially in the matter of staining and washing out. For fixing and preserving the material I have found corrosive sublimate, Flemming's chromosmium-acetic solution, Pereny's fixing fluid, Gram's solution of iodine and absolute alcohol the most useful. The various stains used included

Delafield's hæmatoxylin, Heidenhain's iron hæmatoxylin, methylene blue, fuchsin, methyl green and fuchsin, methyl green and eosin and picro-carmin. The specimens may be mounted whole either in balsam or glycerine or may be first of all sectioned in the microtome, by which certain details of structure can be shown up more clearly.

*The Living Cell.*—In the examination of the living cell under a high power objective it is not difficult to observe that the cell contents are differentiated into two parts, an outer peripheral layer in which the colouring matter is placed, and an inner central part which is colourless. The structure of these two regions is difficult to make out, but both may contain granules of varying sizes, and in some of the larger forms a distinct vesiculate structure can be observed. The outer coloured layer appears in many cases to encroach upon the central portion, which is thereby rendered irregular in outline, but in no case was a penetration of the coloured layer into the middle of the central region observed; in the younger cells near the ends of the filament the central portion is nearly always more regular in outline than in the older cells.

*Cytoplasm.*—In all forms which admit of a careful examination of stained specimens under high powers the structure of the cytoplasm appears to be vesiculate or reticulate, the meshes or alveoli being regularly arranged and somewhat drawn out in the radial and longitudinal directions, so as to give in transverse sections an appearance of trabeculae radiating from the central body to the periphery of the cell (fig. 3). When granules are present these are found in or on the threads, never, so far as I can see, in the meshes of the network. In young vigorous cells the cytoplasm presents uniformly the structure just described, but in old and degenerating cells a very considerable amount of vacuolization is observable in which the central body often becomes involved, so that in such cases no distinction between central body and peripheral cytoplasm can be seen. These vacuolar spaces often contain a slightly coloured sap, probably produced by the breaking down of the colouring matters and their diffusion into the cytoplasm.

*Colouring Matter.*—It has not been possible to obtain any evidence of the existence of a differentiated chromatophore, such as obtains in the higher Algæ, either in fresh or stained specimens, and I am, therefore, quite unable to support Fischer's statement that the central body is surrounded by a cylindrical chromatophore. The colouring matter appears to be contained in minute granules distributed through the cytoplasm in such large numbers as to give the appearance of a uniform diffuse coloration to the whole of the peripheral layer. They appear in many cases to be arranged in regular rows which run slightly obliquely across the cell, and are so clearly defined in some forms as to give the impression that they are contained in definite

fibrils in the cytoplasm. But from a careful examination of the cells of *Phormidium retzii*, in which the coloured granules are sometimes easily seen, it appears to me that they are contained in the threads of the cytoplasmic reticulum only, and that the definite arrangement in rows is due to the uniform and regular distribution of the threads of the reticulum between the central body and the cell wall. Nevertheless the possibility of the existence of a fibrillar structure in some forms is not excluded, and I am not prepared to state definitely that it does not occur.

These coloured granules appear to contain both the colouring matters which are known to occur in the Cyanophyceæ, chlorophyll and anthocyan. Hegler considers them as special organs of the cell, and suggests that they should be called *Cyanoplasts*, but it seems to me that they may very well be compared to the "grana" which are found in the chromatophores of such forms as *Euglena*, diatoms, &c.,\* the difference between them being that in the Cyanophyceæ the "grana" are free in the cytoplasm, in other green plants they are contained in specialised portions of it. This probably indicates that so far as the colouring matter is concerned, we have in the Cyanophyceæ not only a simpler, but also a more rudimentary type of structure than in those forms with a specialised chromatophore or chlorophyll grain.

*The Central Body.*—The central, colourless portion of the cell is considered by many observers to represent the nucleus of the higher plants, by others to be merely a colourless portion of the cytoplasm, or a slightly differentiated portion of it. Whatever it may be it certainly differs in appearance in the living state from the nucleus of the Algae and higher plants, and, in fact, one of the arguments which might be adduced against its nuclear nature is that in the fresh condition it is so very easily seen, whilst the nuclei of some higher forms are very difficult to make out in the living condition. The question of the presence of a nucleus in the Cyanophyceæ is probably one of the most controverted questions of recent years. So long ago as 1879 Schmitz announced the discovery, in the cell of a species of *Gleocapsa*, of a homogeneous, deeply stainable, central mass, which he took to be the nucleus. He came to the conclusion later, however, that this could not be regarded as a true nucleus, but only as a chromatic granule. Scott† and Zacharias,‡ working independently in 1887, came to the conclusion that the central body represents the nucleus of the higher plants. Zacharias was able to make out in some forms which he examined a network-like structure, and demonstrated in it the presence of nuclein, whilst Scott figured structures with a network and

\* See Arthur Meyer, 'Bot. Cent.,' 1882.

† 'Journ. Linn. Soc. Bot.,' 1887.

‡ 'Bot. Zeit.,' 1887.



division stages remarkably like some of the stages in mitotic nuclear division in the higher plants. In a later paper\* Zacharias states that although the central body contains nuclein it cannot be regarded as a true nucleus. Bütschli,† in the same year, on the other hand, comes to a very definite conclusion that the central body is not only nuclear in nature, but that it is the homologue of the nucleus of higher forms. Fischer‡ controverted Bütschli's observations, and stated that the appearances figured by that author are due to a plasmolyzed condition of the cells. In a later paper§ he withdrew this statement, but he still maintained that the central body is not of the nature of a nucleus. Deinega|| was unable to come to any definite conclusion as to the presence or absence of a nucleus. Zukal¶ considered certain granules in the central body to be the nuclei. Hieronymus\*\* considered it to be an open nucleus, and to have a peculiar structure. Palla†† says the central body is homogeneous, and contains no granules. Nadson‡‡ says it is of a nuclear nature. Macallum§§ finds that it contains chromatin, but states that it is not a nucleus, and that there is nothing resembling a nucleus in the Cyanophyceæ. Hegler¶¶ comes definitely to the conclusion that, notwithstanding the absence of a membrane and nucleolus, the central body is a nucleus, and divides by a process of karyokinesis similar to that which occurs in higher plants. Massart,¶¶¶ on the other hand, in 1901, basing his conclusions upon facts observed after staining the cell *intra vitam* with methylene blue, states that not only does it not present the characters of the nucleus of the higher plants, but that it cannot even be regarded as a nucleus of a simpler type.

It is obvious from these various contradictory statements that a considerable amount of caution is necessary in arriving at any conclusion as to the nature of the central body; but I have very little doubt from my own observations that it is of the nature of a nucleus, that it possesses certain of the characteristics of the nuclei of the higher plants, but not all, and that it can very fairly be regarded as a nucleus of a simple or rudimentary type.

\* 'Bot. Zeit.', 1890.

† 'Ueber den Bau der Bacterien, etc.', Leipzig, 1890.

‡ 'Die plasmolyse der Bakterien,' 1891.

§ 'Untersuchungen über den Bau der Cyanophyceen und Bacterien,' Jena, 1897.

|| 'Bulletin Soc. Impér. des Nat.,' Moscou, 1891.

¶ 'Sitzungsb. Kaiserl. Akad. in Wien,' 1892.

\*\* 'Cohn's Beitz. z. Biol. d. Pflanzen,' 1892.

†† 'Jahrb. f. Wiss. Bot.,' 1893.

‡‡ 'Ueber den Bau des Cyanophyceen-protoplastes,' 1895.

§§ 'Trans. Canadian Institute,' 1899.

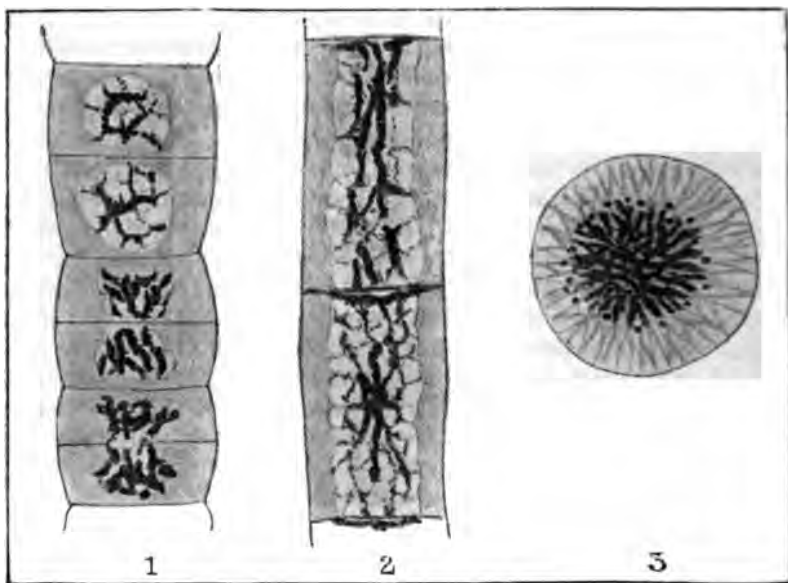
¶¶ 'Jahrb. f. Wiss. Bot.,' 1901.

¶¶¶ 'Sur le Protoplasme des Schizophytes,' Brussels, 1901.

If the cells of any of the larger species of *Cyanophyceæ*, with somewhat elongate cells, be stained with hæmatoxylin, according to the method of Heidenhain, or with a solution of fuchsin, the substance of the central body becomes clearly defined from the peripheral cytoplasm. It does not possess a definite membrane, but in certain cells, generally near the ends of the filaments, it is found inside a vacuolar space in the centre of the cell, so that it is clearly separated from the cytoplasm by the delicate vacuolar layer or membrane (fig. 1). In the older cells this vacuolar space seems to disappear, but in *Tolypothrix*, even in the oldest cells of the filament, it can still be recognised (fig. 2). The central body is usually, in young cells, surrounded on all sides by the peripheral coloured layer, but in some forms, and especially in older cells, it extends from one end of the cell to the other, and is in close contact with the transverse walls (fig. 2), whilst the peripheral coloured cytoplasm forms a cylinder around it. The central body appears in such cases to be intimately concerned in the formation of the cell wall, and is in close connection with the cyanophycin granules which are often found in contact with it in certain species, and which are usually regarded as of the nature of reserve food substances. It seems not unlikely that the central body is concerned in the formation of these granules. In one case which I examined, the central body was almost entirely free from chromatin, whilst the cyanophycin granules, with which it was in close contact, were, contrary to their usual character, stained deeply in hæmatoxylin, the central body being only very slightly stained. I have also obtained a distinct reaction for phosphorus in granules, which by their position and general appearance were cyanophycin granules, whilst the central body gave only a very slight indication of it.

The substance of the central body consists of a more or less regular granular network (figs. 1, 2, 3). The granules are small, and usually uniform in size, but here and there may sometimes occur a granule or granules larger than the rest. The ground substance of the network upon which the granules are placed stains only slightly in nuclear stains, and appears to correspond to the linin or plastin network of the nuclei of higher forms. The granules themselves stain deeply in nearly all the nuclear stains; they resist the action of artificial digestive fluid, and give a distinct, and in some forms a strong reaction for phosphorus when treated according to the method devised by Macallum. They probably, therefore, correspond to the "central substance" of Zacharias, and to those portions of the central body which are found by Macallum to contain masked iron and phosphorus. From a consideration of these facts it is difficult to escape the conclusion arrived at by Macallum that "there can be . . . very little doubt that a chromatin-like substance is present in the central body." And when we further consider the structure of this central body, its

granular network, its definite position, and its delimitation from the rest of the protoplasm inside a vacuolar space, it seems difficult to escape the further conclusion that it is at least to be regarded as a simple type of nucleus.



FIGS. 1 and 2.—*Tolypothrix lanata*: (1) Young, (2) Old cells.

FIG. 3 — *Oscillaria limosa*: transverse microtome section.

*Cell Division.*—The division of the cell is brought about by the formation of a transverse wall which grows inwards from the lateral wall and divides the cytoplasm and nucleus into two equal or nearly equal parts (fig. 1). The division of the nucleus is direct, but it simulates the mitotic figures seen in the higher plants, and recalls some of the features of nuclear division in *Euglena*. It may possibly represent a very rudimentary form of mitosis. As the cell grows in length the chromatin network becomes drawn out in a longitudinal direction and presents the appearance of a number of chromosomes standing side by side. In some cases these threads appear to be actually separate from one another, but on closer examination this appears not to be the case; they are always found to be more or less connected together and retain generally the features of the network as seen in the resting stage. As the new transverse cell wall grows it comes into contact with the nucleus, which thereby becomes constricted as shown in the lowest cell in fig. 1, and the chromatin network then becomes divided into two parts, thread by thread, until in the last stage only one thread may be left, which may persist for some

time connecting the two daughter nuclei together until complete separation takes place (see fig. 2). In some cases, shortly after the division is completed, delicate threads may be observed connecting the daughter nuclei to the new cell wall, and we get then a resemblance to the diaster stage of ordinary karyokinetic division. This is the only indication of the existence of anything like a spindle figure which I have observed in the Cyanophyceæ, and it is not by any means a well-marked or constant feature of the division.

The division of the cell appears to go on independently of the nuclear division. It is quite common to find, long before the first division is complete, several new cell walls in various stages of development in other parts of the cell.

*Theoretical.*—From a careful consideration of the observations contained in this paper it seems clear that, although we cannot regard the central body of the Cyanophyceæ as a nucleus of a normal type similar to the nuclei of the higher plants, it certainly appears to possess a sufficient number of the characteristics of such nuclei to warrant its recognition as a nucleus of a simple or rudimentary type. If we take the chief chemical and morphological characters of the nuclei of higher organisms and compare them with those of the central body, we shall find that it has as much claim to be regarded as a nucleus as some of the structures which are accepted as nuclei in the protozoa. Out of some twelve main characters, chemical and morphological, which are found attaching to the nuclei of higher plants, we have seven, and possibly nine, occurring in the nuclei of the Cyanophyceæ.

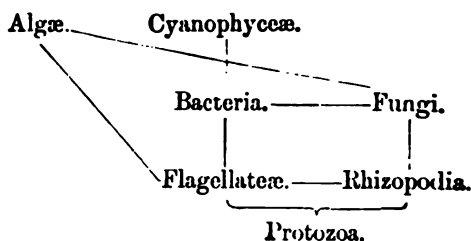
These are: (1) the presence of a nuclear network; (2) its reaction towards nuclear stains; (3) its behaviour towards digestive fluid; (4) the presence of phosphorus; (5) the presence of masked iron; (6) the amitotic division, which resembles, in some respects, the division in *Euglena*; and (7) the presence of chromatin granules on a linin framework. It differs from the nucleus of the higher plants in the absence of a true mitosis with spindle fibres, and in the absence of a nuclear membrane and nucleolus; but under certain conditions the deeply-stained substance of the central body is found condensed into a deeply-stained granule suspended by delicate fibres in the centre of the cell, and in young cells the central body is often limited towards the cytoplasm by a vacuolar membrane, so that the presence, under certain conditions, of a body resembling a nucleolus, and at least a rudimentary nuclear membrane, is not excluded.

If it is not a nucleus then it can only be (1) a specialised portion of the cytoplasm; (2) a body of the nature of a pyrenoid; or (3) a special organ of the cell of which we know not the function.

There seems to me to be no doubt that it is among these plants and in the bacteria and protozoa that we must seek for those types of nuclei which will give us a clue to the most rudimentary condition

of the nucleus; and if we conceive that, in a very rudimentary stage of cell development, the chromatin was diffused through the cytoplasm either in the form of granules or in a liquid condition, then it is not improbable that the accumulation of the chromatin in a single chromatin granule, as in some protozoa, or in a granular network inside a vacuole as in the Cyanophyceæ, would indicate a developmental stage in the evolution of the nucleus.

*Relations of the Cyanophyceæ to other Groups.*—So far as the structure of the cell is concerned, the Cyanophyceæ do not appear to have any very definite characteristics which connect them with any known group of plants, and certainly not with the Algæ. They may possibly be allied to the bacteria with which they appear to have some features in common, but so far as our present knowledge goes their position with respect to other groups is as indicated in the following diagram:—



"Further Observations on the Spectrum of the Spontaneous Luminous Radiation of Radium at Ordinary Temperatures."  
By Sir WILLIAM HUGGINS, K.C.B., O.M., D.C.L., Pres. R.S.,  
and Lady HUGGINS, Hon. Mem. R.A.S. Received October 29,  
1903.

## [PLATE 19.]

In the plate accompanying our paper on the spectrum of the glow of radium bromide,\* at least seven lines are seen to agree, both in position and in intensity, with corresponding lines in the band spectrum of nitrogen. We called attention to other lines, of which some traces may be detected on the plate, and we suggested that with a longer exposure a more complete spectrum would be obtained. One strong line in the radium bromide glow spectrum, about 3914, has no similar line corresponding to it in the band spectrum of nitrogen as given on the plate.

We have since taken photographs, with longer exposures, of two specimens of radium bromide, one prepared by Buchler and Co., and the other received from the Société Centrale de Produits Chimiques. In these photographs, lines only faintly glimpsed in our earlier photographs can be seen distinctly. A photograph taken of the French radium bromide with an exposure of 216 hours, is reproduced on the accompanying plate.

The coincidence of the spectrum with the band spectrum of nitrogen is shown to be even more complete by the presence of a faint trace of the next more refrangible band, beginning at 2976·7. In addition, some of the fainter single lines of the nitrogen spectrum now come out in the radium bromide spectrum.

At the same time that the coincidence down to minuter details with the nitrogen band spectrum is brought out, the strong outstanding line, about 3914, is now seen to be accompanied by a second, but less intense, outstanding line at about 4280; neither of which is present in the ordinary band spectrum of nitrogen, which was the one reproduced on the plate of our first paper.

This nitrogen band spectrum is the one distinguished by Deslandres as that of the positive pole, but it appears at all parts of a vacuum tube, and is also produced when a suitable induction coil discharge, without capacity, is taken across air at the ordinary density. The nitrogen spectrum that was measured by Ames was taken by using an end-on vacuum tube closed with a quartz plate; in his list no lines are given at the places of the two outstanding lines in the glow spectrum.

When, however, the spectrum is taken of the aureole about the

\* 'Roy. Soc. Proc.,' vol. 72, p. 196.

negative pole of a vacuum tube containing a residuum of atmospheric air, the ordinary, or positive-pole spectrum becomes enriched by a new spectrum of bands; and in this additional spectrum the heads of the two strongest bands in the photographic region, occur at the positions of the two outstanding lines of the radium glow spectrum.\* On the plate are given, below the more complete radium spectrum now obtained, the ordinary band spectrum of nitrogen, and also the same spectrum enriched with the bands peculiar to the aureole of the negative pole. This latter spectrum corresponds to that of the radium glow. The peculiar conditions, whatever they may be, which determine the presence of these additional negative-pole bands must find their counterpart in the nitrogen molecules when under stimulation by the radium bromide. The additional bands which show themselves in the spectrum of nitrogen when taken from the glow at the negative pole of a vacuum tube are usually believed to be associated with the stimulation of the very rapidly moving corpuscles of the cathode stream. Accordingly the presence of these negative-pole bands in the spectrum of nitrogen when excited by radium, naturally suggests whether the  $\beta$  rays, which are analogous to the cathode corpuscles, may not be mainly operative in exciting the radium glow. On this surmise it would be reasonable to expect some little extension of the glow outside the radium itself. We are unable to detect any halo of luminosity outside the limit of the solid radium bromide; the glow appears to end with sudden abruptness at the boundary surface of the radium.

It may be that it is only at molecular distances, and at the moment of their formation, that the rays can excite the nitrogen molecules.

As the glow spectrum is produced by the influence of the radium on nitrogen at the atmospheric pressure, it seemed to be of interest to find out whether the negative-pole spectrum could be obtained in air at the ordinary pressure. It has already been stated that when a suitable discharge of an induction coil, without capacity in the circuit, is taken between electrodes in air, the ordinary band spectrum of nitrogen appears. Separate photographs, therefore, were taken of the parts of the discharge in the close neighbourhood of the two electrodes, which were about three-eighths of an inch apart. The bands peculiar to the negative pole of a vacuum tube were found upon the plate taken of the negative electrode.

\* Deslandres' measures, reduced to Rowland's scale, of the heads of these two bands are 3914.4 and 4279.6 ('Thèses,' 1888, Gauthier-Villars, and 'Comptes Rendus,' vol. 101, p. 1256). Angström and Thalén give 4281.6 for the less refrangible band ('Nova Acta Upsal' (3), vol. 9, 1875). Hasselberg's measure for the head of the less refrangible band is 4378.6 ('Mem. de l'Acad. St. Pétersb.,' vol. 32, No. 15). Percival Lewis on "Some new Fluorescence and Afterglow Phenomena in Vacuum Tubes containing Nitrogen" ('Astroph. Journ.,' vol. 12, p. 8) found fluorescent nitrogen to give a band spectrum; and, in some conditions of the fluorescence, the most intense bands were those of wave-lengths 3576.9 and 3371.2.

As the radium glow consists of light from nitrogen molecules stimulated into luminosity by the presence of the more active radium molecules, it was reasonable to suppose that the bromine molecules, chemically associated with the latter, might also be sufficiently stimulated to reveal their presence by the lines in the spectrum peculiar to them. Photographs were accordingly taken of the poles of a vacuum tube containing traces of atmospheric air together with bromine vapour. The band spectrum of nitrogen appeared alone upon the plates when no capacity was introduced; but with the intercalation of a jar, the lines of bromine came out in the photographs, in addition to the lines of air. The experiment was then repeated at atmospheric pressure by enclosing platinum electrodes in a glass bulb communicating with the atmosphere by a narrow tube. Photographs of the coil discharge taken between them revealed the ordinary band spectrum of nitrogen. A few drops of bromine were then introduced into the bulb, filling it with bromine vapour. Photographs were again taken of the discharge in the air now heavily laden with bromine, but the spectrum remained precisely the same as before the bromine was introduced, namely, that of nitrogen only.

We find in this experiment possibly a sufficient reason for the absence of any of the lines of bromine in the glow spectrum: it may be that stimulation from the active radium molecules affects preferentially the nitrogen molecule, so that this molecule can be shaken into luminosity by a stimulation which is insufficient to excite the bromine molecule to a comparable extent.

The experiment then suggested itself whether under similar conditions of discharge, radium itself, when placed upon the electrodes, would be able to show its presence by its characteristic lines in the spectrum of the discharge taken between them. The result was negative, as in the case of bromine, no lines other than those of nitrogen appearing upon the plate. A small jar was then put into the circuit and another photograph taken, when the complete spectrum of radium came out strongly, but without the band spectrum of nitrogen.

If, as suggested by Rutherford, the  $\alpha$  rays are connected with helium, the experiment seemed worth making of taking a photograph of the spectrum arising from their bombardment upon a zinc sulphide screen. It seemed possible, though not very probable, that the encounters of these bodies, at the enormous speed at which they travel, with the molecules of air, and their final collision with the screen, might on that hypothesis give rise to some of the radiations peculiar to helium and so produce its spectrum on the plate. Fortunately the strong continuous spectrum due to the fluorescence of the screen ends abruptly in the violet a little before the place, at 3889, of the strongest line of helium in the photographic region, and so leaves the spectrum quite free for the detection of this line, even if it were only faintly present. The result



of the experiment, so far as concerns helium, was negative; which must not of course be interpreted as excluding the presence of helium, but only as showing that, if present, the conditions are not favourable to the appearance of its spectrum.\*

On the first photograph that was taken, the two strongest lines of the nitrogen band spectrum were faintly seen, but a photograph with a new screen and a longer exposure showed no trace of the nitrogen bands. In the first case it might be, that some very minute particles of radium bromide had attached themselves to the screen, and by their independent glow had given rise to the lines of nitrogen which were on the photographic plate.

About 1 centigramme of French radium bromide, which was in the form of small particles, was put into a very small glass tube scarcely larger than was necessary to contain it. The tube was securely closed and left for 2 months. As the  $\alpha$  rays, being unable to escape, would probably occupy the interstices between the radium bromide particles, it seemed desirable to examine whether as helium, or still in some precedent condition, they would show their presence in the glow spectrum. The tube was exposed, immediately in front of the slit, for 168 hours. The spectrum shows a strong continuous spectrum from the fluorescence of the glass, and faintly the bands of nitrogen, but no other lines with certainty. We intend to photograph again the spectrum of the glow from this tube, after a longer time has passed for an accumulation of the  $\alpha$  rays, and of the gas-like emanation.

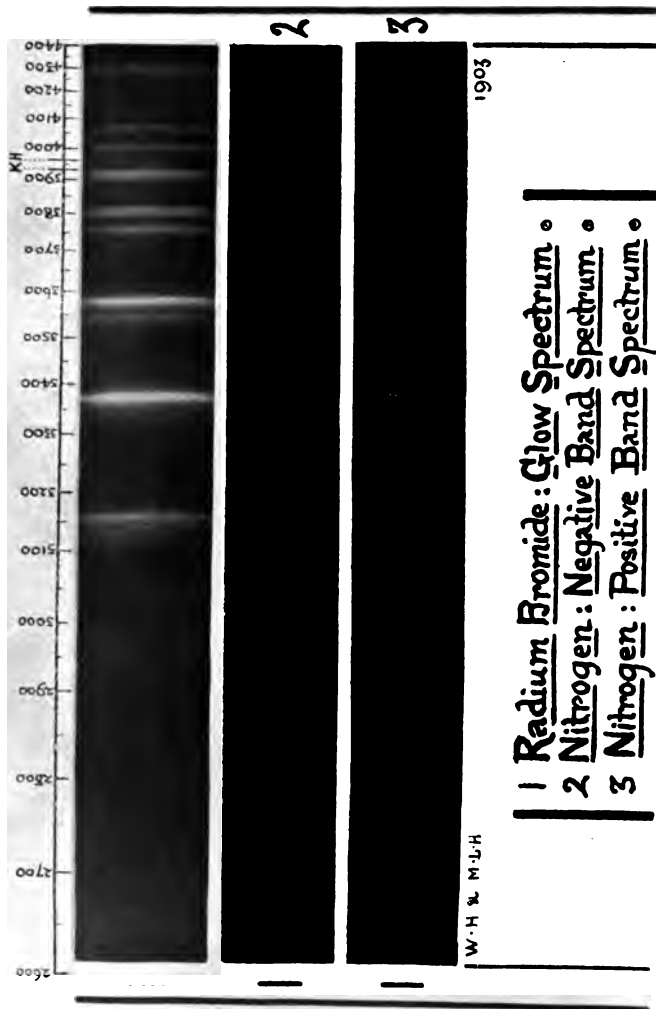
When the radium bromide is covered with a plate of quartz, the continuous spectrum, due to the fluorescence of the quartz, is not only strong, but extends a long way into the ultra-violet. It can be traced on the photograph as far as 2500.

After a few hours the quartz darkens under the action of the radium bromide, the brown stain extending through the complete substance of a plate one-tenth of an inch in thickness. The stain is due probably to the reduction of silicon.

Experiments were made in the hope of throwing light upon the shift found in the photograph of the radium glow spectrum, reproduced on the plate of our first paper. As subsequent photographs of this spectrum were entirely free from any trace of shift, the shift found on the first plate must have been accidental. Repeated photo-

\* M. Henri Becquerel has quite recently investigated the scintillation observed on a phosphorescent screen when excited by radium. He comes to the conclusion (1) "Ce sont les rayons  $\alpha$  qui provoquent la phosphorescence scintillante"; (2) "Ces faits établissent sinon une démonstration, du moins une grande présomption en faveur de l'hypothèse qui attribuerait la scintillation à des clivages provoqués irrégulièrement sur l'écran cristallin par l'action continue plus ou moins prolongée des rayons  $\alpha$ ." ('Comptes Rendus,' vol. 137, pp. 632, 634; October 27, 1903.)

# Spectra of Radium Bromide and of Nitrogen





graphs, taken with the spectroscope in different positions, failed to show the smallest trace of shift from flexure. The only suggestion we can make in explanation is that the piece of solid radium bromide accidentally shifted in its cell, so as no longer to be directly under the slit, and in consequence the collimator lens was not wholly filled with light.

The results of the experiments described in this paper would appear to show generally, if analogy with electric stimulation may be assumed, that the radium stimulation, whether we take the operative cause to lie in the  $\beta$  rays, or in the encounters of nitrogen molecules with the active molecules of radium—by which, for the first time, a spectrum of bright bands in the ultra-violet region has been obtained at ordinary temperatures, and without the intervention of an electric discharge—from the very circumstance of its being of such a nature as to give rise to the band spectrum of nitrogen, is not of a kind which can elicit from either the molecules of bromine, or of radium their characteristic line spectra.

The question suggests itself whether or not the same inability may hold in respect of the helium molecule, which is easily stimulated by an electric discharge; we have not as yet made experiments on this point.

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“Correction to Paper ‘On the Spectrum of Radium.’” By  
Sir W. CROOKES, F.R.S. Received November 9, 1903.

The faint line 3961·624, described\* as a radium line, is due to aluminium, being one of the strongest lines in the Al spectrum. Its wave-length, recently measured on a special aluminium photograph, shows the identity; moreover, with a pure salt of radium it is found to be absent.

\* ‘Roy. Soc. Proc.,’ this volume, p. 300.

"On the Rapidity of the Nervous Impulse in Tall and Short Individuals." By N. H. ALCOCK, M.D. Communicated by A. D. WALLER, M.D., F.R.S. Received October 20,—Read November 19, 1903.

(From the Physiological Laboratory, University of London.)

### *Introduction.*

While the effect of varying conditions on the rapidity of transmission of the nervous impulse has been fully studied, no research has yet been made as to whether the stature of the individual and the corresponding difference in the lengths of homologous nerves has or has not any influence on this rapidity, and as recent work has rendered it desirable that the question should be considered, the research here recorded was undertaken to this end.

Two series of observations were made: (1) On the frog; (2) on man.

### Series I.—ON FROGS' NERVES.

The following plan was adopted after several preliminary trials:—Two frogs differing in size were taken, and measurements made of the length from nose to anus, and of the sciatic from the emergence of the last nerve root to the gastrocnemius muscle. Gastrocnemius-sciatic preparations were then made, and placed side by side so that the nerves rested on a little hollow metal platform which was covered with thin sheet indiarubber, while the muscles were fixed just outside this. Crossing this platform were two pairs of electrodes, 20 mm. apart, and the two nerves lay across these, so that each nerve could be simultaneously excited at either pair of electrodes. The platform was covered by a hollow lid, and iced water was passed through both lid and platform, so that the nerves were equally cooled to about 0° C., while the muscles remained at room temperature (17—19° C.). The muscle twitch was recorded on a rapidly moving drum in the usual way. This method presents the advantage that while the nervous impulse is equally reduced in both nerves to an easily measureable speed, the delay due to the end-plates and muscles remains at its normal figure, any alteration in this latter factor bears, therefore, a lesser ratio to the total "latent period" than in experiments where both nerve and muscle are at ordinary temperature. The excitation was maximal throughout.

FIG. 1.

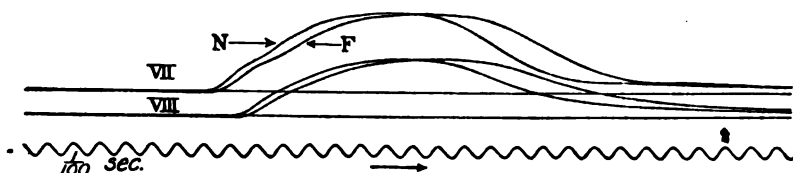


FIG. 1.—Frogs VII and VIII. Simultaneous record of twitches. N = excitation from "near" pair of electrodes. F, from "far."

## Experiments.

|                   | Length of<br>frog. | Length of<br>sciatic. | Observed<br>time. | T° C. | Rate<br>of impulse. |
|-------------------|--------------------|-----------------------|-------------------|-------|---------------------|
|                   | mm.                | mm.                   | secs.             |       | m. per sec.         |
| Frog I. ....      | 67                 | 45                    | 0·0042            | +1°·5 | 4·8                 |
| " II. ....        | 50·5               | 36                    | 0·0038            | ..    | 5·3                 |
| " III. ....       | 74                 | 49                    | 0·0024            | -0·2  | 8·3                 |
| " IV. ....        | 45                 | 30                    | 0·0026            | ..    | 7·7                 |
| " V. ....         | 71                 | 50                    | 0·0038            | +0·3  | 5·3                 |
| " VI. ....        | 55                 | 35                    | 0·0036            | ..    | 5·6                 |
| " VII. ....       | 75                 | 46                    | 0·0028            | +0·8  | 7·1                 |
| " VIII. ....      | 53                 | 33                    | 0·0030            | ..    | 6·7                 |
|                   |                    |                       | ±0·001            | ..    | ±0·2                |
| Mean of 4 long .. | ..                 | 48                    | 0·00330           | ..    | 6·07                |
| " 4 short..       | ..                 | 33·5                  | 0·00325           | ..    | 6·12                |

From these measurements it is clear that the rapidity of the nervous impulse *per unit length* is the same in all the frogs examined. As the total length of the sciatic varied from 50—30 mm., the time taken to travel from the central to the peripheral end was, therefore, proportionately longer in the larger frogs.

## Series II.—ON MAN.

The method adopted was that elaborated by Waller.\* A sensitive "Sandström" air tambour was connected by flexible tubing to a hollow rubber cylinder held in the hand, so that the contraction of the flexor muscles of the fingers would compress the cylinder. The excitation was by break induction shock to the median nerve, the anode† being applied (1) above the clavicle; (2) at the bend of the elbow internal to the biceps tendon, the kathode being applied on any

\* Waller, A. D., 'Exercises in Practical Physiology,' Part III, p. 63.

† This position of the electrodes was found to give more concordant results than the usual practice of placing the kathode over the nerve.

convenient spot. The movement of the lever of the tambour was recorded on a pendulum myograph, this serving to open the break key in the primary circuit in the usual way. The strength of excitation was 6000 units of the standard Berne coil, worked by a 4-volt accumulator.

This method presents the advantages of a muscle-nerve preparation in a perfectly normal condition, and with a length of available nerve from 290—380 mm., but requires the most careful attention to detail. It is necessary by preliminary experiments to ascertain (1) that the rate of the pendulum is invariable within the limits of error required; (2) that the break shock occurs always at the same place on the plate; (3) that the height of each contraction as recorded by the tambour shall be approximately the same; and (4) to use the same tambour and length of tubing throughout the series of experiments.

FIG. 2.

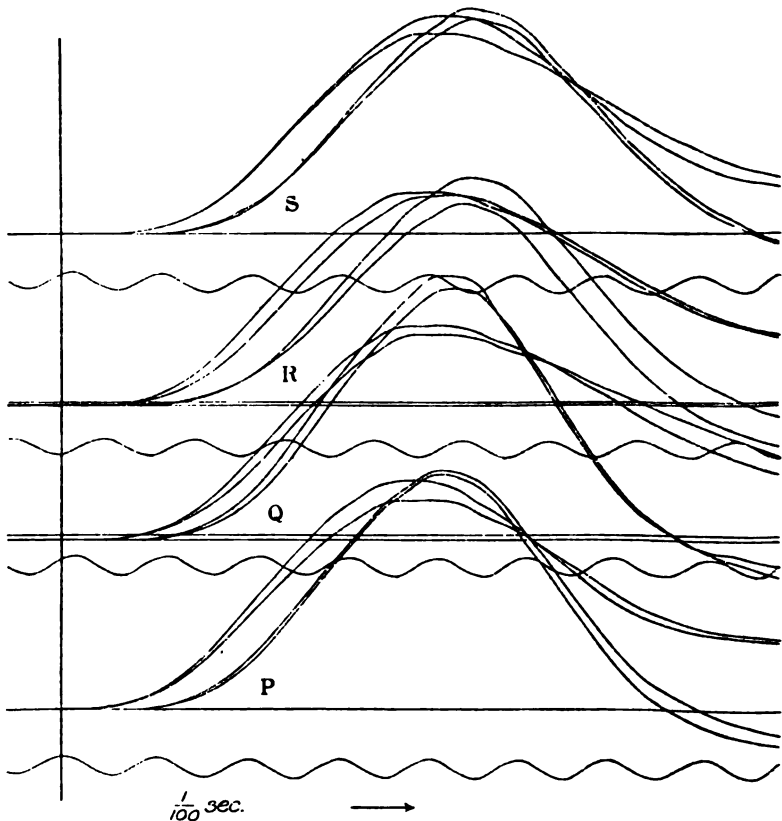


FIG. 2.—Subject C.D. Four consecutive experiments. Each consists of a pair of "near" and a pair of "far" excitations.

In order to keep a check on the experiments, these were made in two pairs (except in subject AB), two contractions of "near" excitation and two of "far" being superposed, any accidental error of any one contraction could be thus detected by the non-congruence of the curves.

It was found possible to obtain with care four or five consecutive experiments on the same subject without error in any one case greater than  $\pm 0.0001$  second from the recording apparatus (fig. 2).

The reading of the time difference between the "near" and "far" curves presents some difficulty owing to the gradual rise of the lever at the commencement of the curve. In order to check my own readings, I asked Dr. T. G. Brodie to re-measure several of my curves, and his independent readings have agreed with mine within the limit of error of  $\pm 0.0001$  second.

#### Experiments.

| Subject.                                                                 | Height. | Length of nerve. | No. of experiments. | Mean value observed. | Rapidity of nervous impulse in metres per sec. |
|--------------------------------------------------------------------------|---------|------------------|---------------------|----------------------|------------------------------------------------|
|                                                                          | mm.     | mm.              |                     | sec.                 |                                                |
| Tall. { Short. {<br>AB, age 21<br>CD, age 20<br>EF, age 32<br>GH, age 22 | 1758    | 290              | 7 (single)          | 0.0044               | 66.5                                           |
|                                                                          | 1684    | 295              | 15 (double)         | 0.0046               | 65.8                                           |
|                                                                          | 1844    | 380              | 6 (double)          | 0.0056               | 67.7                                           |
|                                                                          | 1930    | 360              | 12 (double)         | 0.0054               | 67.3                                           |
|                                                                          |         |                  |                     |                      |                                                |

The results on the human subject agree with those obtained from the frog, namely, that *per unit length*, the rate of the nervous impulse is the same in all individuals examined, and the consequence follows that the time taken to traverse the limb nerves in a tall man is appreciably longer than in a short man. In the subjects examined, this difference was 0.001 second approximately, and if the reaction time to touch from the hand or foot were measured, this would—*cæteris paribus*—be from 0.003—0.004 second longer in the taller individuals, a distinct penalty to pay for their greater stature.

It will be observed that the mean velocity, deduced from the total number of forty experiments, is 66.8 metres per second ( $\pm 0.1$ ), a figure that is rather higher than that originally given by Helmholtz\* and more recently by Waller.†

\* Helmholtz u. Baxt. 'Monatsb. d. Berl Ak 1867 s. 228 (1870, s. 184).

† Waller, *loc. cit.*



*Observations.*

The results here recorded have an additional theoretical interest when considered in connection with the recently published work of Boycott.\* This observer showed that in the sciatic of the frog the number of nodes of Ranvier is very approximately constant, and is independent of the length of the frog (33·2 in twenty-six frogs), and that the length of the internodes differs considerably, ranging from a length of  $1803\mu$  in large frogs to  $249\mu$  in small. *Per unit length* therefore there are many more nodes of Ranvier in the sciatic of a small than in that of a large frog, and as the present measurements show that the rapidity of the nerve impulse is the same in both classes of frogs, it follows that *the nodes of Ranvier are without any influence on this rapidity*, and that the internode cannot be regarded in the light of a functional unit in this connection.

As the length of the internode is proportional, both to the length of the whole nerve and to its diameter, it is not unreasonable to infer that this visible pattern furnishes a scale by which the invisible ultra-microscopic structure of the nerve-fibre can be estimated. It has been shown above that the scale of the visible pattern is without effect on the rate of the nervous impulse, it follows that the size of the invisible structure is also without effect, and this will modify such theories of nerve propagation as take this latter into account.

It gives me much pleasure to acknowledge the kind advice and assistance I have received from Dr. Waller in the prosecution of this research, and also to return my thanks to the gentlemen who lent themselves to the purpose of my experiments.

*Conclusions.*

- (1) The rapidity of the nervous impulse *per unit length* is the same whatever be the stature of the individual.
- (2) The time taken by this impulse to travel from the centre to the periphery is greater in taller individuals.
- (3) The nodes of Ranvier exercise no influence on the rate of impulse.

\* Boycott, 'Journal of Physiology' (in the Press).

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“On the Physiological Action and Antidotes of Colubrine and Viperine Snake Venoms.” By LEONARD ROGERS, M.D., B.S., M.R.C.P., F.R.C.S., Indian Medical Service. Communicated by Dr. A. D. WALLER, F.R.S. Received and read November 19, 1903.

(From the Physiological Laboratory of the London University.)\*

(Abstract.)

#### Part I.—COLUBRINE VENOMS.

The Indian Colubrine snakes other than the Cobra have been little investigated since the classical work of Fayrer, Lauder Brunton and Wall. Their physiological actions are dealt with in this paper.

I. The *Naja Bungarus* or Hamadriad is the largest poisonous snake. The symptoms produced by it are identical with those of Cobra venom, and its toxicity is very similar in degree to it.

Its hæmolytic action is very slight compared to that of the Cobra, its power in this respect being only about one-hundredth that of the latter.

Blood-pressure and respiratory curves of this and the other venoms dealt with in this paper have been taken in the case of cats and rabbits by means of a Gad's manometer connected with a cannula in the carotid artery, and a Sandström recorder connected with a tracheal cannula, with the following results :—

In Experiment I a dose of 5 milligrammes per kilogramme produced paralysis of respiration in  $1\frac{1}{2}$  minutes, followed by circulatory failure of a secondary nature in 2 minutes. In Experiment II 1 milligramme per kilogramme produced a temporary stimulation of respiration followed by complete failure in 10 minutes. In Experiment III a very similar result was obtained, while, in addition, it was found that by means of artificial respiration the circulation could be kept going long after total cessation of breathing. In each case the motor end-plates of the diaphragm were paralysed at the end of the experiment, but by means of stimulating the nerve at intervals during the experiment it was found that this paralysis did not take place until after that of the respiratory centre.

The action of Hamadriad venom then, in all respects, resembles that of the Cobra, with the exception that it has very little hæmolytic action.

II. The *Bungarus fasciatus* or Banded Krait, although a large snake, has always been considered the least deadly of its class in India. The symptoms which it produces are very similar to those of the rest of

\* A grant in aid of this research was received from the Royal Society.

the class, only in addition it may cause a chronic affection. This difference I find is due to its containing some of the Viperine element in addition to the Colubrine one, and it may thus produce intra-vascular clotting in large doses. The blood-pressure and respiratory tracings show the typical respiratory paralysis of Colubrine venoms, but in addition it causes a marked primary fall of blood pressure, while artificial respiration fails to keep the circulation going, as with the other Colubrine venoms. Heating to 90° C. for a short time greatly lessens this effect on blood pressure and renders artificial respiration much more efficacious, owing to the Viperine element being more readily destroyed by heat than is the Colubrine one. The venom also produces motor end-plate paralysis like the other Colubrines.

III. The *Bungarus ceruleus* or Krait is a small but deadly snake. The symptoms produced by it are identical with those of Cobra venom, and a blood pressure and respiratory tracing shows that it paralyzes the central respiratory centre in the same way as the latter. Its action on the phrenic end-plates is, however, somewhat less marked than that of the other Colubrines.

We see, then, that each of these venoms causes death by paralyzing the respiratory centre just like Cobra and Sea-snake venoms, but in addition the venom of the Banded Krait has a Viperine element which produces a primary fall of blood pressure, and sometimes intra-vascular clotting, thus resembling the Australian Colubrine snake, the *Pseudochis porphyreus*.

Calmette's antivenin has an undoubted specific action against Cobra venom. It, therefore, becomes a matter of practical importance to ascertain if it is also effective against the other Colubrine and Sea snakes, whose lethal action is identical with that of the Cobra. A series of experiments have been carried out by mixing about ten times a fatal dose of venom with different quantities of the serum for half an hour before injection and noting the results. It was first tested against the common variety of the Cobra, which it neutralised more readily than it did the venom of a less common kind. It acted next best against the Hamadriad or King Cobra, and only a little less so in proportion to its toxicity, against the *Enhydrina bengalensis*, a Sea snake. In the case of the Krait its action was much more feeble, although still distinct, while in that of the Banded Krait it prevented all Colubrine symptoms, if a sufficient dose was used, but the animals died 2—4 days after with symptoms of chronic Viperine poisoning, thus confirming my conclusion that this venom is a mixture of the two elements.

These results are of great interest in showing that the serum has a definite action in neutralising the respiratory paralyzing poison of all the Colubrines and the Hydrophidæ, although it will require to be made stronger than it is at present, if it is to be relied on to cure the bites

of those snakes against whose venoms it has the lesser degrees of action, and those which eject a very large quantity of venom. I would suggest that a more generally useful antivenin might possibly be prepared by using a mixture of different Colubrine venoms in the preparation of the serum.

## Part II.—THE VIPERS AND PIT-VIPERS.

A. *The Viperidae*.—I. The *Daboia Russellii* produces intra-vascular clotting in small animals, and loss of coagulability of the blood in man, accompanied by hæmorrhages from the bowel, etc. This latter chronic form of poisoning can also be induced in smaller animals by first giving small subcutaneous or intra-venous doses to produce the negative phase of reduced coagulability of the blood, and then larger lethal amounts. As I found that in this way quite rapid deaths without any intra-vascular clotting could be caused by intravenous injections of the venom, accompanied by remarkable primary failure of the circulation, I have made a prolonged investigation of this phenomenon, using the venoms of two Vipers and two Pit-vipers, with results of considerable interest. The direct application of stronger solutions of the venoms than those used in the experiments when applied directly to frogs' hearts, did not stop their action, while in many of the blood-pressure tracings it was evident that the heart continued to beat regularly during and long after the pressure fall. When the pressure fall was sufficiently rapid to stop the respirations by cutting off the blood supply of the medulla, on the occurrence of respiratory convulsions of asphyxial origin the blood pressure was frequently pumped up again in a remarkable manner and the respirations recommenced. Further, the increased excursions of the pulse during the fall of pressure, and the common occurrence of marked Traube-Hering curves, pointed to a relaxation of the blood-vessels of vaso-motor origin.

In order to ascertain if the fall in pressure was due to a central vaso-motor paralysis, further experiments were carried out with *Daboia* venom. In Experiment VIII the spinal cord of a dog was cut in the cervical region, and artificial respiration kept up. A subcutaneous followed by an intravenous dose of the virus was injected, and no sudden fall of pressure occurred, and the heart continued beating for some minutes, proving that the falls previously obtained were not due to direct action of the venom on the heart. In Experiment IX the circulation in the omentum was observed to undergo a very marked vaso-motor dilatation coincidently with the usual fall in blood pressure, while, after this was complete, no further persistent fall occurred when the cervical cord was cut, proving that complete paralysis of the central vaso-motor centre had already taken place. Lastly, a record of the portal blood volume changes, due to the amount of blood entering the vessels of a large loop of small intestine placed in an oncometer, were

recorded simultaneously with the general blood pressure in the carotid artery, and marked vaso-motor dilatation was observed to take place coincidently with the fall in the general blood pressure, instead of a passive diminution in its volume, which should have taken place if the circulatory failure had been due to a direct action on the heart itself.

That the vaso-motor affection was central, and not peripheral, was shown by the fact that both a small dose of Daboia venom (and also a large one of Cobra) produced contraction of the vessels of the limbs through which blood was transfused after separation from the influence of the central nervous system, while adrenal extract and nicotine caused marked elevation of the blood pressure of a temporary nature after complete paralysis of the central vaso-motor centre, as shown by a stimulation of the central end of the sciatic nerve failing to produce any rise of the general blood pressure.

II. The African Puff-adder. This venom (for which I am indebted to Dr. J. W. W. Stephens) produces intra-vascular clotting like Daboia venom in small animals, but it is much easier to produce the negative phase of lost coagulability, and thus produce death without any clotting with it, than with Daboia venom itself. The blood-pressure and respiratory curves in such cases resemble in every important essential those of Daboia venom without clotting. Adrenal extract has the same effect in raising the fallen pressure, as does nicotine, which was suggested to me by Sir Lauder Brunton. Further, a very marked vaso-dilatation of the portal circulation in a loop of the small intestine, coincidently with the fall in the general blood pressure, was recorded. The Puff-adder venom also had a very marked effect in producing petechial hæmorrhages in the peri- and endo-cardium, and in the mesentery and omentum in particular, which is not at all an important feature of Daboia poisoning.

B. *Crotalidae*. I. *Crotalus horridus*, or Rattlesnake: I am indebted to Dr. J. Brunton Blaikie for this venom, the hæmorrhagic symptoms produced by which are well known. Blood-pressure and respiratory tracings of the action of this venom showed that the same primary failure of the circulation, as in the former instances, is produced by it, but without any intra-vascular clotting, except rarely at the seat of injection. The failure of the respiration appears to be secondary to that of the circulation, while the very feeble action of strong solutions of the venom directly on the heart will not account for the facts observed, including the pumping-up of the blood pressure with the occurrence of respiratory convulsions and well-marked and persistent Traube-Hering curves, as with the other Viperine venoms. In this case, again, the dilatation of the vessels of the portal circulation, coincidently with the general fall of blood pressure, has been both observed under the microscope and demonstrated with the oncometer.

Further, artificial respiration fails to improve the circulation after respiratory failure, while, in the primary respiratory failure of Colubrine poisoning, it is most effective.

II. *Trimensurus anamallensis*, the Indian representative of the Rattlesnake class has also been examined (thanks to the kindness of Dr. W. Dowson), with precisely similar general results to the others, the same vaso-motor paralysis being induced by a small single intra-venous dose without any intravascular clotting, as in the case of the Rattlesnake, while, in larger doses, it kills with intra-vascular clotting like the true vipers. It has much less effect in causing hæmorrhages than either the Rattlesnake or the Puff-adder, but less than the Daboia.

Thus we find from a comparison of the action of these four Vipers that while in the case of the two Pit-vipers a primary circulatory failure, quite independent of any intra-vascular clotting, can be readily induced by a single intra-venous dose of the venoms, the same result can also be brought about in the case of the two true Vipers by first producing the negative phase of reduced coagulability by preliminary small doses of the venoms. Further, there are cases on record of complete loss of clotting power for several days, in which ultimate recovery took place, while the hæmolytic changes, which are produced by all these venoms, are not of lethal intensity. The failure of respiration is always secondary to that of the circulation, while none of these venoms have any marked direct paralyzing action on the heart which could account for the circulatory failure.

On the other hand, we find a complete paralysis of the vaso-motor centre in the medulla is common to all these venoms, and will fully account for the lethal effects found, although in some of them the hæmorrhagic effects will greatly aid it. If my conclusion is correct that the essential action of the Viperine poisons as a class is a paralysis of the central vaso-motor centre, just as the Colubrine class paralyse the respiratory centre, then it would appear to be possible to produce an antivenin against the former venom on the same lines as Calmette's serum against the Colubrine class, a mixture of Viperine poisons being used for injections. In the meantime such drugs as adrenal extract and nicotine, together with cardiac tonics, may be of material value in doubtful borderland cases, in keeping up sufficient blood pressure to insure a sufficient supply of blood to the medulla to maintain the respiratory centre working.

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**CROONIAN LECTURE.**—"The Cosmical Function of the Green Plant." By C. TIMIRIAZEFF, Professor of Botany in the University of Moscow. Communicated by Sir M. FOSTER, Sec. R.S. Received April 30,—Lecture delivered April 30, 1903.

[PLATES 20—22.]

The first object which attracted Gulliver's notice when on his visit to the Academy of Lagado was a man of "meagre appearance," his eyes fixed on a cucumber sealed in a phial. On Gulliver's questioning him, the strange personage explained that for more than 8 years he had been absorbed in the contemplation of this bit of apparatus, trying in vain to solve the problem of the storage of the sun's rays in this recipient and their possible utilisation.

Now, to begin with, I must frankly confess that I am just that sort of man: for 35 years have I been staring, if not exactly at a cucumber in a phial, still at what comes to the same thing, at a green leaf in a glass tube, and breaking my head in vain endeavours to clear up the mystery of "bottled sunshine." If I venture to bring before this illustrious Society the modest results of this long-continued work—it is in the hope that this theme may have a real, though very distant connection with the subject which Dr. Croon, the generous and enlightened founder of this lectureship, considered as most fit for the occasion. During a long series of years the chief topic of these lectures was "Muscular Motion," and at a more recent period "Motion in Animals and Plants," and "The Origin of Vital Movements" in general. Perhaps I may be allowed to take a step further in this direction—in fact, the last possible step, and speak of the energy manifested in all these movements, of its remotest source—the sunbeam stored in the green plant.

I suppose it is hardly necessary to remind you that the ground we are going to tread has been explored in this country and America for more than a century. Suffice it to call to mind the familiar names of Priestley, Count Rumford, Daubeny, Sir David Brewster, John William Draper, Sir John Herschel, Robert Hunt, Sir George Gabriel Stokes, Mr. Edward Schunck, Mr. Sorby, Sir William Abney, Mr. Blackman, and last—not least—Mr. Horace Brown, to show what interest this question has continued to inspire under its various aspects. I may add that it was in Professor Tyndall's brilliant "Heat a Mode of Motion" and in my resultant study of Robert Mayer's classical work "*Die organische Bewegung in ihrem Zusammenhange mit dem Stoffwechsel*," that I found the first impulse towards all my subsequent work. And must be admitted that the moment was singularly propitious:

Bunsen and Kirchhoff had just discovered that powerful means of research—spectrum analysis; Sir George Stokes had applied it to the study of the colouring matter of blood; Desains and Tyndall had worked out Melloni's thermoscopic methods; Henri Sainte-Claire Deville had made his great discovery of the dissociation of carbon dioxide; Bunsen, by simplifying the methods of gas analysis, had quite recently put them at the disposal of the physiologist, and lastly, Boussingault had just published his classical researches on the assimilation of carbon, showing that this process could be easily studied on leaves or even on pieces of leaves detached from the living plant.

From the very outset, on the first page of my first Russian paper, which appeared in 1868, I formulated the problem in all its generality in the following lines: "To study the chemical as well as the physical conditions of this process, to follow the solar ray that effects it directly or indirectly, up to the moment when we see it vanish on being transformed into internal work, to find out the quantitative relation between the energy absorbed and the work done—here lies the brilliant though perhaps arduous problem in attacking which modern physiologists ought to unite all their forces."

And I may now add that the very moderate results obtained after a long series of years only confirm that, at all events, I did not overrate the difficulties of the problem.

When I first set to work, the current idea was that the photochemical process going on in the green leaf under the influence of light ought to be considered a function of its luminosity. This belief was chiefly based on J. W. Draper's classical experiments on the spectrum. From a theoretical point of view it seemed to me highly improbable that a chemical process so essentially endothermic, and consequently depending on energy of radiation, should stand in a direct relation to a purely physiological property of radiation, having no existence outside the organ of sight. Light, taken in the narrow acceptance of the word, does not exist for the vegetable world. But facts brought forward by such an authority in this line of research as Draper were not to be so easily dismissed on the single ground of their improbability. However, a careful study of Melloni's classical memoir on the shifting of the maximum of heat with the state of purity of the spectrum, brought me on the track of a considerable experimental flaw in Draper's researches. His spectrum was highly impure; in fact it was obtained by means of a circular aperture  $\frac{3}{4}$  of an inch in diameter—Wollaston's narrow slit not seeming to be in general use at the time. A sufficient explanation was thus obtained for the coincidence of the chemical effect with the maximum luminosity in the yellow and green rays, this part of the spectrum being practically white, slightly tinged with these colours, and consequently acting by



the sum of nearly all the rays of the spectrum, its limits only remaining monochromatic.

The next step was to prove that this coincidence of the two maxima of luminosity and of the chemical effect did not in reality exist. A simple inspection of these three curves (the curve of assimilation, that of luminosity and the energy curve), taken from my first (and last) German paper, proves with sufficient evidence that a coincidence of the chemical effect with Fraunhofer's luminosity curve was out of the question; but, so far as the visible spectrum is concerned, there exists a decided relation with the energy curve.

In this first and preliminary research the more simple and convenient method of coloured liquid screens, introduced by Senebier and applied in a more exact form by Daubeny, was adopted. I merely introduced a more correct way of calculation and graphical representation of the results obtained. At the same time I applied the method of gas analysis now in general use, though quite erroneously attributed to Professor Pfeffer.

But if these results were sufficient to dispose of the current ideas on the importance of the luminosity, based as they were on Draper's experiments, they were not sufficient for the building of another theory. It was impossible, for instance, to consider the decomposition of the carbon dioxide as simply an effect of the relative energy of the radiation. The maximum of energy in a prismatic spectrum lies in the infra-red, and a remarkable experiment of Cailletet (curiously too often omitted in most of the historical sketches of the subject) gave an unequivocal proof that the rays of light, filtered through Tyndall's solution of iodine in carbon bisulphide, were incapable of producing the reduction of the carbon dioxide in a green leaf.

It was evident that some other principle had to be brought forward in order to explain the absence of any chemical action in the invisible part of the spectrum, as well as its distribution in the visible. The principle that was appealed to was Sir John Herschel's law: that a photo-chemical reaction may be induced by those rays only that are absorbed by the substance undergoing a change and consequently, as a rule, presenting a complementary colour. It was supposed that, applied to our case, Herschel's law would mean that the reduction of the carbon dioxide must take place at the expense of those rays of the spectrum which are absorbed by the green matter of the leaf—that they must correspond to the absorption bands of chlorophyll. \*

Lommel is generally credited with having been the first to enunciate the idea that the reduction of the carbon dioxide may be considered as a function of the energy of radiation and of the degree of its absorption by chlorophyll. But this opinion, despite its being very general, is none the less erroneous. Lommel himself admits that the first half of the proposition, concerning the dependence on the energy

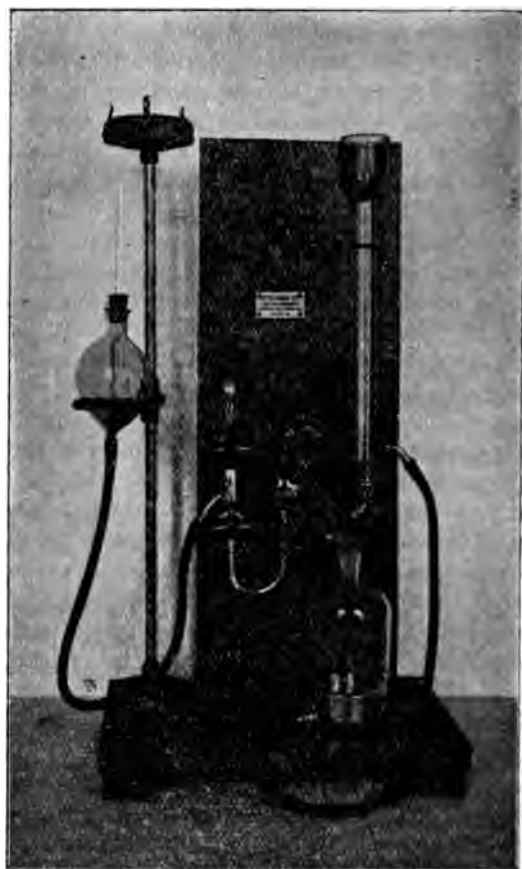
of radiation, was formulated by me, and I may add that I could not affirm the second half of the truth for the simple reason that it had already been affirmed before me, and consequently before Lommel, by Jamin and Edmond Becquerel. It is only a matter for wonder that, as a physicist, Lommel was not acquainted with Jamin's well-known text-book and the perhaps still better known book of Becquerel "*La Lumière, ses Causes et ses Effets.*"

But of course the main thing was not to express an idea, however exact, but to furnish an experimental proof of its exactness. *Nullius in verba* is now, as it was centuries ago, the watchword of every man of science. In other words, it was necessary to repeat Draper's celebrated experiment without falling into his error, and there was the chief difficulty. It is generally admitted that this proof was furnished for the first time by my old friend Professor N. Müller, but I am sorry to say that on this point I am again obliged to contradict the general opinion. In fact Müller never furnished the direct proof of this connection between the chemical process and the absorption of light, and he could not do so because he did not possess the only means of escaping Draper's error. In his first work, previous to my researches, he experimented in a tolerably pure spectrum, but the light intensity was then insufficient and he could not actually obtain any reduction of the carbon dioxide, but only inferred that it took place, judging by the differences in the intensity of the respiration. In his second paper, which appeared after my publication, he could affirm directly the reduction of carbon dioxide, but only at the cost of the purity of his spectrum. In fact the width of his slit was nearly the same as in Draper's experiment, and the result was practically the same; this time he obtained the maximum effect in the yellow rays.

If I allow myself to insist on this point somewhat in detail it is not from any vain desire to establish my priority, but because it is my firm conviction that the method adopted by me is now, as it was at that time, the only means of avoiding Draper's error. Müller did not devise any means of avoiding and consequently had no chance of escaping it. The dilemma, as fully exemplified by Müller's failure, was the following: if the spectrum is pure the intensity of light is not sufficient to obtain a reduction of carbon dioxide; if, on the contrary, we open the slit in order to increase the intensity of the spectrum, we may be sure beforehand of obtaining the maximum effect in its middle, somewhere in the yellow or green rays. There was but one means of escaping the two horns of this dilemma—it was to increase the intensity by diminishing the dimensions of the spectrum; but then the leaf surfaces being reduced in proportion, the quantities of gas to be analysed would be too small to be measured in such gasometric apparatus as the chemist of the time could put at the disposal of the botanist.

The main object was to alter, so to speak, the scale of the **gasometric** measurements without altering the precision of the **method** and the convenience of all the operations. Though I have often since that time changed the details, the principle of the **method** I adopted remains the same. The leaves are introduced into cylindrical tubes of suitable diameter, or still better into flat tubes in order to increase the

FIG. 1.



green surface, and the gases are measured and analysed in a tube of the smallest possible bore. All the necessary manipulations, the transfusion of gases as well as the treatment by liquid re-agents, are easily performed by using this form of gas pipette, which I introduced in 1871, and still (fig. 1) consider the most convenient. The gas pipette and the mercury trough are rigidly connected, allowing us to give to the ascending branch of the syphon an outer diameter not exceeding

1.5 mm., so that it may be easily introduced into eudiometers of 2 mm. inner diameter. This method has also the advantage that no stopcock or rubber is used.

All the necessary manipulations may be thus briefly summed up; thanks to this modified form of Bunsen's gasometer, the necessary gas mixture on its way through this burette is, so to speak, cut into slices of suitable volume and distributed to the leaves in the flat tubes. After the necessary exposure to the spectrum the gases are extracted by means of the pipette just described, and introduced for analysis into these eudiometric tubes, which easily allow the estimation of 1/1000 of a cubic centimetre.

Thanks to all these contrivances, the problem of obtaining trustworthy analytical data with green surfaces exposed to a pure spectrum was for the first time solved, and I still consider this method the only one that may be safely relied upon in the study of this question. The two other methods that have been proposed are far less exact. Counting the number of gas bubbles emitted by small aquatic plants, which may be demonstrated as a pretty lecture-room experiment, even if their diameters are measured under the microscope, as recently proposed by Kohl, is hardly to be recommended. It is true, we may obtain much better results when using what I call my *microeudiometer*—a small piece of apparatus which permits us to measure and analyse in a couple of minutes a bubble not bigger than a pin's head. Though reduced here to a minimum, the sources of error inherent in the aquatic nature of the plant are still not fully eliminated.

As to the third method, Engelmann's well-known bacterium method, I still consider that it is of rather too indirect a character, and persist in my opinion, expressed many years ago, that chemical problems ought to be studied by chemical means. Moreover, we shall presently see how little this method is to be relied upon.

Thus we see that the introduction of a gasometrical method allowing the measurement and analysis of very small quantities of gas made it for the first time possible to study the assimilation of carbon in a pure spectrum.\*

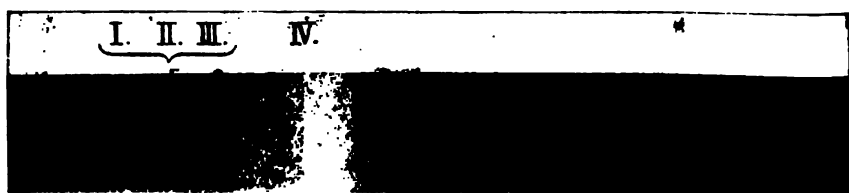
There were two more points to be considered before handling this problem of the connection between the photo-chemical process and the absorption of light in the green leaf. The spectra of chlorophyll and

\* In order to illustrate the difficulties I had to contend with, I may quote one of the best authorities in this line of research, M. G. Lemoine. Speaking at so recent a date as 1895 ('*Annales de Chimie et de Physique*,' Ser. 7, vol. 6, December) of his experiments on the decomposition of oxalic acid in sunlight, M. Lemoine says: "*Les expériences devraient être faites, non seulement avec la lumière blanche, mais encore avec ses différentes radiations. En pratique, il est impossible de les isoler complètement, et si on le pouvait, on n'aurait plus assez d'intensité pour des mesures quantitatives.*" My method may be thus summarised: a heliostat with the largest mirror and a gas burette of the smallest bore.

of its nearest products had to be studied more thoroughly than they had been. It would lead me too far out of the way if I were to give an account of my researches published in a small Russian volume in 1871. My plates represent an attempt at a classification of chlorophyll and its products based on their spectroscopic characters, an attempt that seems to me fully confirmed by the more recent and detailed researches, especially of the late Mr. Edward Schunck, of Marchlevsky, and of Professor Hartley. I will pause for one moment on the method of representing the spectra which I adopted at the time and have since been trying to improve. Till then the spectrum was generally represented as consisting of distinct black bands separated by bright intervals, and it corresponded to a certain more or less arbitrary state of concentration or thickness of layer. Plotting together whole series of spectra corresponding to layers of varying thickness, I obtained the following spectrograms. At a later period I substituted, for a somewhat troublesome method, the direct inspection of the solutions in wedge-shaped troughs—a method, if I am not mistaken, introduced by the late Professor Gladstone—and lastly contrived to obtain directly these spectrophotograms. It is a curious fact, to be mentioned *en passant*, that so far as I know photography has till now been applied only to the more refrangible and not to the less refrangible part of the spectrum of chlorophyll, which is of the highest interest to the botanist.

Here are some photographs that I obtained, in 1892 (fig. 2), on ordinary Ilford plates, which were also used for the first spectrophoto-

FIG. 2.



Photographic Spectrum of Chlorophyll.



Modified Chlorophyll (Stokes), same Concentration.

grams of 1895, but now I prefer Cadett's excellent spectrum plates. The most convenient form of this wedge-shaped cell for photographic use is the following (fig. 3, A). A cubical glass cell is divided by a glass partition into two prismatic compartments, one of which is filled with the coloured solution, the other with the solvent. A horizontal slit is, on the whole, preferable, since it permits us to alter easily the concentration of the solution so as to obtain the desired spectrogram, and the swing-back of the camera may be used for focussing the spectrum. In these photo-spectrograms (fig. 3, B) we have, of course, the most convenient way of representing absorption spectra, but we shall see later that in certain cases we shall still be obliged to have recourse to another method—the spectrophotometric.

Returning now to our chief problem, we may see how important it was to know the real form of the absorption curve. All the spectra generally represented being discontinuous, showing sharp bands alternating with light intervals, it was rather puzzling to account for the continuous effect, as for instance, in Draper's experiments.

Armed with the necessary gasometric and spectroscopic methods of research, I could at last repeat Draper's classical experiment without the fear of repeating his error. The result of my experiments was a strict confirmation of the applicability of Sir John Herschel's law to our case. Not only do the two maxima coincide (fig. 4), but the assimilation curve reproduces very nearly the absorption curve, so far at least as the less refrangible part of the spectrum is concerned. It is to be remarked that the secondary maxima of absorption seem to have no effect, but it is subject to doubt, especially after the latest researches of Schunck and Marchlevsky, whether they appertain to the principal chlorophyll constituent or to some products of its decomposition.

The same results were obtained later by quite another method. The dissociation of carbon dioxide represented by this curve (fig. 4), the "photolysis," as it may be called, is the first and by far the most important stage of the whole process, being directly dependent on the external source of energy. But it is closely followed by the photosynthesis of organic matter. Though, thanks to the brilliant researches of Horace Brown and Morris, we now know that starch is neither the first nor by far the only product of this synthesis, still it is a product that follows the reduction of the carbon dioxide at the short interval of some minutes, and, what is of still greater importance, its presence may be easily shown by the well-known iodine test.

If the reduction of carbon dioxide be considered a function of those waves of light which correspond to the chlorophyll absorption bands, and, on the other hand, the production of starch is the next stage of the same photo-chemical process, it may be fairly presumed that this production of starch in a spectrum will be strictly localised, restricted

FIG. 3.

A.

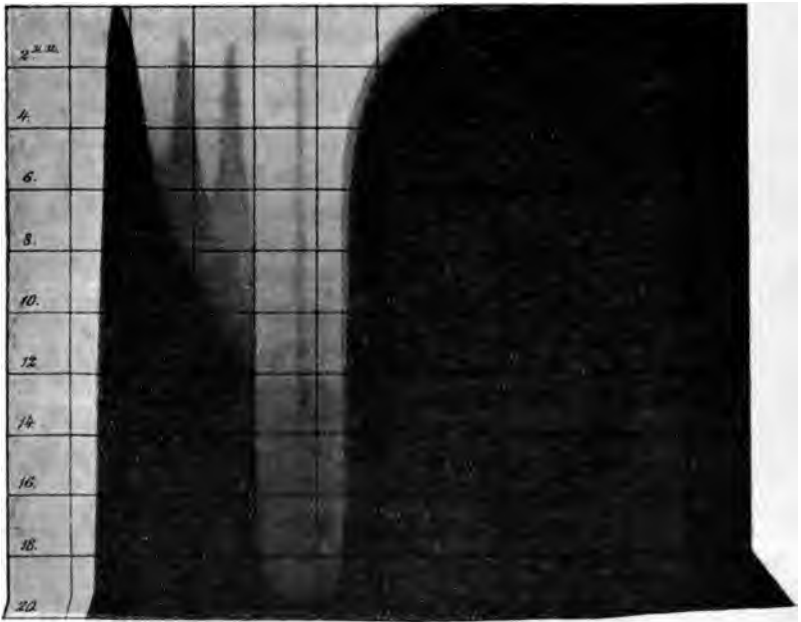
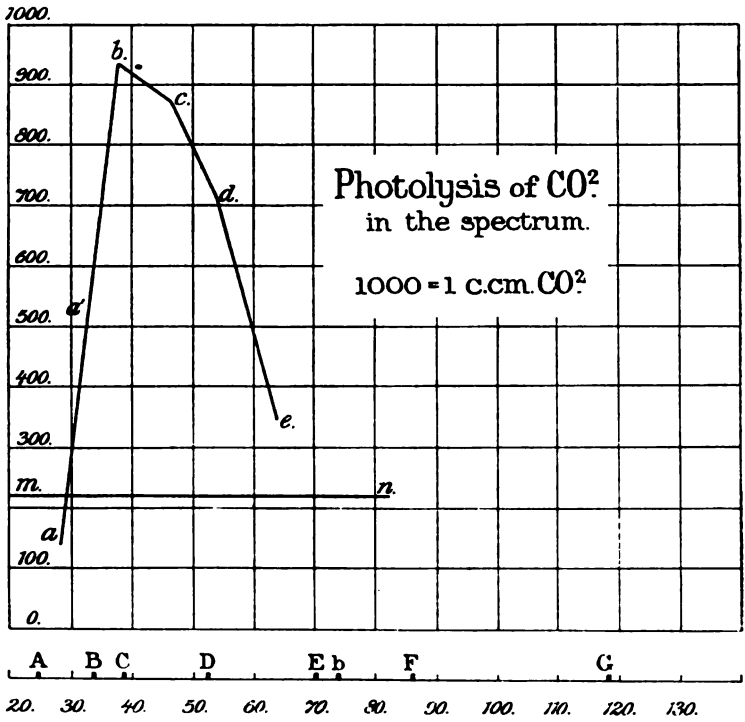


B.



Apparatus for taking Photographs and the direct Projection of Spectrograms  
with the Lantern.

FIG. 4.

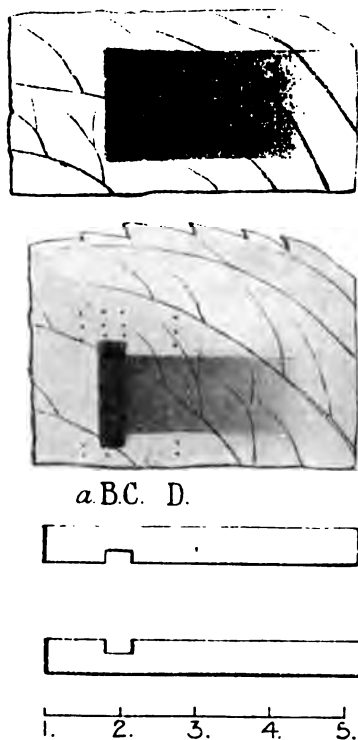




to the absorption bands of chlorophyll. In other words, a spectrum of sufficient intensity, projected on a living leaf previously depleted of its starch, will impress in this leaf an invisible image of the chlorophyll absorption spectrum formed of starch grains. This latent image may be developed by the iodine test.

These previsions have been fully realised in the following experiment. Healthy leaves attached to the living plant (a *Hydrangea*) but previously deprived of their starch, after an exposure of 5—6 hours to the influence of a small but very bright and pure spectrum, were treated in the well-known way with an iodine solution. They exhibited a well-defined spectrum of chlorophyll with its principal band between B and C very prominent, and a gradual falling off towards the blue end (fig. 5). Just as in the case of the reduction curve, no secondary bands could be detected.

FIG. 5.

Photosynthesis of  $C_6H_{10}O_5$  in the Spectrum.

The blue and violet rays produced hardly any effect. This last result may be chiefly attributed to the fact that the appearance of

starch is only the resultant of two conflicting processes, of its production and its dissolution, so that at a certain point when the assimilation is not sufficiently intense the former may be counter-balanced by the latter, no surplus starch being stored in the chloroplast.

This leads us to the discussion of the very important question concerning the relative effect of the rays of the more refracted part of the spectrum. It might have been remarked that my researches were restricted to its less refracted half.

Concerning the other half, the current opinion was that these rays play a comparatively small part in our photo-chemical process. This opinion was considered the result of Draper's classical experiments and of a great many experiments with yellow and blue coloured screens. But all these latter experiments are little to be relied upon, since it may be proved by photo-metrical measurements that the intensity of the transmitted light is diminished in very different proportions by these media, and that in consequence the results obtained are not directly comparable. And they are likewise unreliable when the prismatic spectrum is used, because of the great dispersion of these rays, and that was the reason why I confined myself to the less refrangible half of the spectrum and did not push the experiment further into the blue and violet rays. It may be shown, by-the-by, how capricious and unreliable in this respect are the results obtained by Engelmann's bacterium method. It will suffice to put *en regard* the results obtained by Engelmann and those of one of his most faithful adherents—Professor Pfeffer. In the former case we have a distinct second maximum corresponding to the blue rays—in the latter no such maximum could be observed.

It might seem that the defect inherent in the spectrum method might be easily remedied by a simple calculation, assuming that the effect is proportional to the intensity. But the law which regulates the relation of the process to the intensity of light not being known, this assumption would be gratuitous, and in fact we shall see later that this law is much more complicated.

The simplest experimental way of solving the question would, of course, seem to be to make the experiment in a diffraction spectrum. But a series of experiments I made with a beautiful Rowland grating gave only a negative result—just as in Müller's first experiments—the light intensity not being sufficient, no reduction of the carbon dioxide could be directly revealed. In consequence, I was obliged to fall back on the prismatic spectrum. I may, perhaps, be allowed to refer to the fact that even Mr. Langley, notwithstanding the wonderful sensitiveness of his bolometer, remarks in one of his latest papers, "The prism is, on the whole, far more convenient than the grating."

To work with the prism, care being taken to avoid the error arising from the differences of dispersion, was in this case simply to adopt the

well-known method used by physicists for recomposing the prismatic spectrum. We may thus combine the intensity of the prismatic spectrum with the advantages of the diffraction spectrum, the gasometric results being directly comparable. I used the very ingenious apparatus devised by the late Jules Dubosq for the production of complementary colours. It consists of a cylindrical lens and of a wedge-prism fixed on a plate of glass. Instead of a spectrum we obtain two stripes of light of equal area and of complementary colours.

More recently I proposed a modification of this apparatus (skillfully executed by M. Pellin) consisting of two glass plates with their respective prisms, which may be made to slide past one another and divide the spectrum into three parts (see Plate 20, A, *b*).

The glass tubes containing the leaves being immersed in mercury (Plate 20, A, *a*), the spectrum must of course be divided in the vertical sense, but in other cases it may be more convenient, as will be presently seen, to adopt Kundt's method of dividing it in the horizontal sense so that the two coloured surfaces may be put into direct contact (Plate 20, B, *c*). As I have just said, this method combines the advantages of the grating and of the prism, the difference of dispersion being eliminated as in the diffraction spectrum, the intensity remaining the same as in the prismatic.

Moreover, in this last respect the method may present even an advantage over the simple prismatic spectrum. If desirable the spectrum used may be in a considerable degree impure (that is, obtained by means of a broad slit), provided the stripes of light to which the leaves are exposed are of a homogeneous colour and present equal areas. We have but to place behind them a small Sorby-Browning spectroscop (Plate 20, B, *a*) with a scale giving the wave-lengths, and notwithstanding a certain degree of overlapping of the portions of the spectrum corresponding to the coloured stripes, the analytical results may be directly plotted on a normal spectrum scale. Thus, thanks to this method, not only the error arising from the difference of dispersion, but even if desirable a certain degree of impurity of the spectrum, may be easily done away with and the maximum intensity of light obtained. I may add that I still prefer using a pure spectrum.

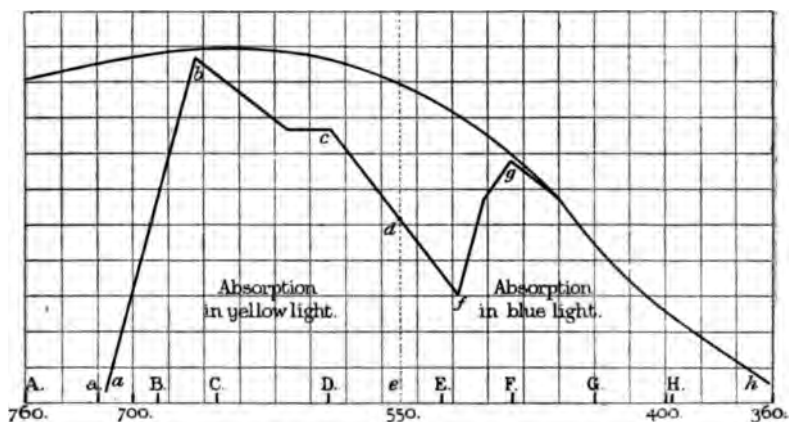
The experiment undertaken to find the relative effect of the two halves of the spectrum was conducted in the following manner. A beam of light reflected by a large Foucault heliostat (furnished by M. Pellin) (fig. 9), and condensed on the slit by means of a lens of 25 cm. diameter, was decomposed by a direct-vision prism and recomposed into these two complementary bands of yellow and blue light. If we admit that the limits of the effective rays in the visible spectrum correspond to the wave-lengths of 700 and 400 millionths of a millimetre, a line passing somewhere about the wave-length 550

will divide our spectrum into two halves with reference to the diffraction spectrum. The analytical results obtained may consequently be directly compared and plotted on a diffraction spectrum.

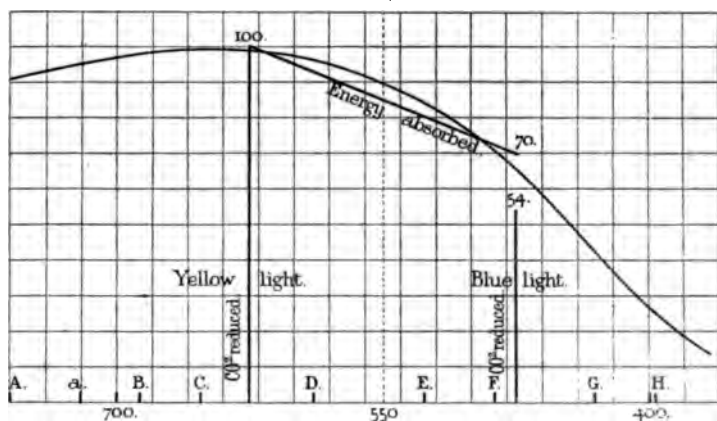
They may be stated thus: if the quantity of carbon dioxide reduced in the yellow half be represented (as a mean of six experiments) by 100, the effect of the blue half will be 54 (fig. 6B). The principal

FIG. 6.

A.



B.



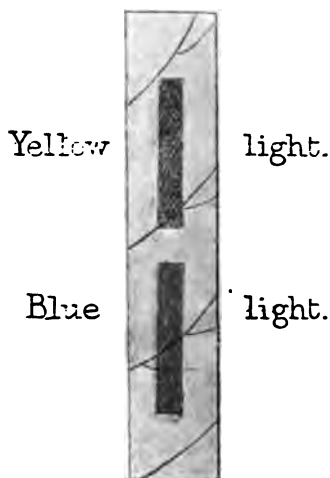
result is that the effect of the blue and violet rays has been till now somewhat underrated.

The same result has been obtained with regard to the iodine starch test, the spectrum being divided as just described in the horizontal sense in order to have the two surfaces directly superimposed (fig. 7).

Whilst in the spectrum as we have just seen (fig. 5), the blue and violet rays produced hardly any effect, here the effect of these rays was quite prominent.

The fact that the reduction of carbon dioxide as well as the production of starch is due to the rays absorbed by chlorophyll, may be

FIG. 7.



thus considered as fully established in all its details, the more so that an elaborate bolometric study of the chlorophyll spectrum in the infra-red by Donath, has proved that there are no absorption bands in this region. This accounts for the fact established, as we have seen, by Cailletet, that no reduction can be attributed to the rays filtered through Tyndall's iodine solution.

We have now to consider the second of the two points mentioned above concerning the connection between the photo-chemical process and the absorption of light. We have seen that Jamin, Edmond Becquerel and, lastly, Lommel, expressed the opinion that Herschel's

law might be applied to our case. But it seemed to me that in this reasoning there was a certain logical flaw, a link missing, between the premisses and the conclusion deduced. Herschel's law means that the photo-chemical effect is confined to those rays of light only which are absorbed by the substance undergoing chemical change. Sir John Herschel applied it himself to chlorophyll, showing that this substance underwent a process of bleaching in exactly those rays of the spectrum which correspond to the absorption bands.

But in the reduction of carbon dioxide we have quite a different case—the substance undergoing decomposition is a colourless gas and light is absorbed by another substance, chlorophyll. It was decidedly impossible to see in this case a direct application of Herschel's law, and that was one reason the more for my not insisting on this point at the beginning of my researches. But the same reason accounts for my being one of the first to acclaim the importance of Professor Vogel's beautiful discovery of *optical sensitisers*.

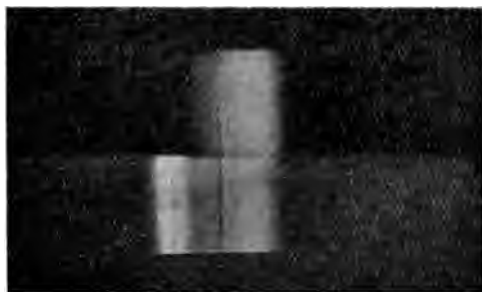
This brilliant achievement not only revolutionised the practice of photography but furnished at the same time that missing logical link, the absence of which did not permit of Herschel's law being applied to the case of the green leaf. Vogel's researches on Eosine were shortly followed by Edmond Becquerel's experiments on collodion plates

sitised by an admixture of chlorophyll, so that in less than a year or the publication of my first experiments I was able to give them a rational explanation in the light of Vogel's new theory. This idea, that chlorophyll plays in the living organism the part of an optical sensitiser, which I advanced for the first time in 1875, is now generally accepted, but I suppose very few botanists have had an opportunity of seeing the photographic effect of chlorophyll on a sensitised plate. I lately Edmond Becquerel in 1877 kindly showed me his beautiful collodion plates; but the collodion process being now somewhat out of fashion, I tried to find a simple way of applying the sensitising action of chlorophyll to the gelatino-bromide plates now in general use.

Alcoholic solutions are not practicable in this case, and I found it very convenient to substitute a potassium or sodium chlorophyllate, which is easily soluble in water.

Here is a plate (Ilford ordinary), half of which has been immersed in a bath of chlorophyllate of sodium, and then exposed to a spectrum filtered by means of a yellow filter to its least refrangible part (fig. 8).

FIG. 8.



B.C. D.

It may be seen that whilst on the ordinary plate the effect stops short of the line D., in the part that has been immersed in the sensitising bath there is a bright band corresponding exactly to the principal absorption band of chlorophyll between the lines B. and C.

I tried to push the analogy between the effect of chlorophyll in a sensitised plate and in the green leaf a step further, by showing that chlorophyll is an optical sensitiser, not only in Vogel's but in Sir William Abney's acceptance of the word.

Sir William Abney admits that an optical sensitiser is as a rule a sensitive dye, *i.e.*, one that rapidly fades in the light. Sir John Schell's classical researches on the bleaching of paper tinged with chlorophyll, prove that chlorophyll belongs to the above class. I have

here a chlorophyll print of a fern leaf. The leaf was applied to a plate coated with a film of collodion tinged with chlorophyll. After a short exposure to direct sunlight we observe that the whole ground is bleached, the parts protected by the leaf retaining their original hue. The image is fixed by a short immersion in a bath of copper sulphate. On submitting such chlorophyll collodion plates to different rays of the spectrum, I convinced myself that this bleaching effect is due to the same rays which effect the reduction of carbon dioxide.

I may perhaps be allowed to dwell a little longer on this important question of chlorophyll playing the part of a sensitiser. The sensitisers are in general divided into two groups—chemical and optical. The former are considered simply absorbents of one or more of the products of the reaction, the latter are at the same time absorbents of radiant energy. An optical sensitiser is supposed to be at the same time a chemical sensitiser, but the reverse of course does not hold good. The existence of chemical sensitisers was admitted long before Vogel's discovery; many instances of their action may be found in Becquerel's well-known book, and in consequence at a very early date, in 1871, in my Russian work "Spectrum Analysis applied to Chlorophyll," I admitted that chlorophyll may be considered a sensitiser in the purely chemical acceptance of the word. I insisted that the reduction of carbon dioxide being essentially a process of dissociation, and the "rapidity of dissociation depending on the removal of the products of dissociation," "the plant acts as an absorbent, continually disturbing the equilibrium between the carbon dioxide and the products of its dissociation," and finally that we must probably admit "the existence of two modifications of chlorophyll somewhat corresponding to hæmo- and oxyhæmoglobin of the blood, the latter being perhaps capable of originating a product analogous to carbonyl hæmoglobin."

At the time it seemed to me that these two states of oxidation corresponded to the normal green chlorophyll and to Sir George Stokes's modified chlorophyll (fig. 2), my experiments having put it beyond doubt that the latter was the product of oxidation of the former; but later I discovered another reaction of chlorophyll, which I look upon as highly important from the physiological point of view we are now considering. When a moderately concentrated solution of chlorophyll is acted upon by hydrogen in the nascent state, it is transformed into a substance nearly colourless, or of a pale yellow hue, but possessing a beautiful purple colour when highly concentrated. This substance can exist only in a total absence of oxygen. On being brought into contact with air it almost immediately recovers its natural green colour. The spectrum of this reduction product of chlorophyll (I proposed to call it protochlorophyllin, or simply protophyllin) in a diluted state, is characterised by a total absence of bands in the less

refrangible part of the spectrum, but when sufficiently concentrated, it shows a very distinct band nearly corresponding to the II band of chlorophyll and another band about the place of the IV, no traces of the principal band I being present. It was the first case of a product of chlorophyll characterised by the total absence of what had been considered the principal characteristic of the chlorophyll spectrum. It is evident that we have here a reduced constituent of chlorophyll, from which chlorophyll is regenerated almost instantaneously on its being brought into contact with the oxygen of the air.

Having obtained these important reactions of reduction and regeneration of chlorophyll in its solutions, I took all possible pains to find out the existence of this protophyllin in the living plant. The formation of chlorophyll in etiolated seedlings being a process of oxidation (the fact was demonstrated in my laboratory by Dementieff in 1873), it was quite natural to search in etiolated seedlings for this protophyllin so easily convertible into chlorophyll on being oxidised. The facts exposed in the current literature were rather discouraging, the so called *Etiolin* of the German botanists always presenting the characteristic chlorophyll spectrum. My first steps were also unsuccessful. I obtained, it is true, solutions where the second band was rather more pronounced; in some cases it had even the same intensity as the first band, but I looked in vain for solutions in which the first band would be totally absent, until the idea struck me that the precautions generally taken were not sufficient to eliminate completely the influence of light. I inclosed the small pots with the seeds that were intended to germinate (sunflower seeds proved to be best) in tin cases, which in their turn were kept in a cupboard in a photographer's dark room. The solutions were prepared in the same dark room, all the precautions used in orthochromatic photography being taken. The result was that I obtained solutions of protophyllin without the least traces of the chlorophyll spectrum.

The colouring power of these solutions being very small, they had to be studied in tubes 50 cm. long. In general about ten or twenty cotyledons were used for preparing the necessary solution for filling the tube. But it was sufficient to expose a single cotyledon, or even a part of one, for an instant to the light in order to obtain a solution that would present the characteristic chlorophyll bands. These facts suffice to prove that in the living plant there exists a colouring matter with the properties of reduced chlorophyll, almost instantaneously convertible into chlorophyll on being exposed to light.

Of course it would be of still greater importance to obtain a direct proof of the presence of this reduced constituent of chlorophyll in the green leaf; this fact alone could account for its playing the part of a chemical sensitiser; but the detection of this substance in the green leaf must needs present certain difficulties. As I have just insisted, the



solutions of protophyllin possess a colouring power greatly inferior to that of chlorophyll, so that their presence may be easily disguised by the latter. Thus assuming that this reduction of chlorophyll actually takes place in a green leaf, it will hardly be manifested by a change of colour or of the spectrum, but simply by a diminution in the intensity of the green hue, by a certain bleaching of the green parts exposed to the light. Now this bleaching effect has in fact been often observed, but was generally attributed to the migration or change of volume of the chloroplasts—a supposition that seems to me highly improbable when applied to the palisade-parenchyma, especially when the rays of light do not fall strictly in the direction of the cell axes. I really think that at any rate the greater part of this bleaching may be accounted for by supposing some of the chlorophyllin to be reduced to protophyllin. To sum up, we may thus admit the existence not only of two, as in the blood, but even of three states of oxidation of the green colouring matter. These transformations may be considered a starting point for a theory of chlorophyll as a chemical sensitiser.

Having enumerated the chief arguments in favour of the admission that chlorophyll may be considered a sensitiser in both acceptances of the word—a chemical and an optical sensitiser, an absorbent of the products of reaction as well as an absorbent of the active rays—I will try to take a step further and show that it may be considered not only one of the innumerable representatives of the group, but a substance quite exceptionally adapted to this function.

At the very outset of my researches I was impressed with the idea that such an intensely endothermic reaction as the dissociation of carbon dioxide, must needs stand in some relation to the energy of the radiations involved in the process. At the time we had no direct knowledge of the distribution of energy in the spectrum, but I pointed out that researches in the diffraction spectrum might possibly alter the current notions concerning the relative calorific effect of the different radiations and prove that the greatest energy should be attributed, not to the dark infra-red rays, but to a certain group of rays in the visible spectrum—possibly the same that are absorbed by the green plant, so that the two maxima—of energy and of chlorophyll absorption—may after all coincide.

My previsions were fully confirmed by the brilliant researches of Mr. Langley and Sir William Abney. I called attention to this foreseen coincidence in a small note in the 'Comptes Rendus' shortly after the appearance of Mr. Langley's classical paper. My statements of these facts being still contested, the correctness of my quotations being even suspected by Professor Engelmann, I feel myself bound to bring forward the original data. In Sir William Abney's paper in the 'Proceedings of the Royal Society' for 1887, it is shown that the maximum of energy corresponds to the wave-length about two-thirds between 600 and

700 millionths of a millimetre, let us say 666 (a figure easily retained in the memory, it being the number of the Beast). The maximum of absorption is somewhere about the two-thirds between the lines B. and C., between 686 and 656, consequently again about the wave-length 666-millionths of a millimetre. At a later date Mr. Langley furnished data which I have plotted above (fig. 6, A and B), and we shall soon have occasion to apply them. It must be remembered that Mr. Langley's numbers refer to what he calls "high sun." For the mean intensity of the whole day the coincidence would probably be still closer. We may consider the same question from another point of view. I have made a rough attempt to represent the relative amplitudes of the vibrations corresponding to the different rays of the spectrum, and it may be seen that the greatest disturbances correspond to that region of the spectrum where the principal absorption band of chlorophyll, and therefore the maximum chemical effect on the carbon dioxide, are situated.

But we may perhaps find a still more convincing argument in favour of the supposition that the photo-chemical effect of a radiation is a function of its energy, in a comparison of chlorophyll with the other sensitisers, and still more in a comparison of the relative effects of yellow and blue light in the experiment just cited.

There is an important fact, based on the testimony of such able observers as Eder and Vogel, and made especially conspicuous in a very elaborate paper of Mr. Acworth, the fact that the two maxima, the maximum of absorption of light by the sensitiser and the maximum of photographic effect on the sensitised plate, do not strictly coincide—the latter, as a rule, being shifted towards the red end of the spectrum. No explanation has been put forth for this fact, nor does Mr. Acworth offer any, holding at the same time that the fact in itself is past any doubt. But so far as chlorophyll is concerned a curious error seems to have crept into Mr. Acworth's statements. He admits that chlorophyll makes no exception to the general rule, *i.e.*, that the maximum of chemical effect does not correspond to the maximum of absorption in the first band but is shifted to the red end of the spectrum—though an attentive glance at the figure relating to chlorophyll will easily convince one that there is something wrong about it. As in the other cases, Mr. Acworth gives the two curves, the absorption curve and the curve of the sensitising effect on the photographic plate, in order to show the shifting of the latter towards the red end of the spectrum. But in fact his statement (in both text and figure) concerning the absorption spectrum of chlorophyll is inexact. Here are his very words: "Die Absorption dieser Emulsion ist, was die Haupt- und weniger brechbare Bänder betrifft, deutlich ausgeprägt. Dieses beginnt etwas vor C., erreicht bei C $\frac{1}{3}$ . D. ein Maximum; jenseits desselben ist die Absorption nicht hinlänglich scharf zu verfolgen, um sie genau zeichnen zu können."

Now, it is a fact testified by thousands and thousands of observations that the principal chlorophyll band lies between B. and C. and not between C. and D. On the contrary, Acworth's curve representing the sensitising effect has its maximum between B. and C.—nearer to C.—exactly where innumerable observations unanimously place the principal absorption band of chlorophyll, and in this respect all we know only confirms the exactness of Mr. Acworth's experiment. Beginning with the late Edmond Becquerel's first experiment and ending with my recent photographs, we always see the maximum of the sensitising effect corresponding to the band between the lines B. and C. It follows that Mr. Acworth places the maximum of photographic effect in the right place, but the maximum of absorption in an evidently wrong place, and it is only by means of this evident error that chlorophyll is made to agree with the general rule.

In reality the two points perfectly coincide, and as a further consequence chlorophyll must be considered an exception to the general rule of the shifting of the maximum of chemical effect towards the red end of the spectrum. Now it seems to me that the exception as well as the rule might find an explanation in the simple admission that the photo-chemical effect must be attributed not only to the degree of absorption of a certain group of rays of which the band is composed, but at the same time to the energy or the amplitude of the corresponding vibrations. In every absorption band (in the limits of the visible spectrum) the side nearer to the red end will be composed of radiations possessing a greater amount of energy, and as a consequence of the supposition just made, the maximum effect must be shifted that way until we arrive at that part in the red where the maximum of energy and absorption coincide. At this point there will be no reason for any shifting of the photographic maximum, and so we get an explanation of the curious anomaly presented by chlorophyll as a photographic sensitiser.

Of course the *experimentum crucis* for testing my hypothesis would be, using Sir William Abney's wonderful method of infra-red photography, to see whether in the infra-red part of the spectrum Acworth's rule would be reversed. But this kind of research is quite out of the reach of a botanist.

Meanwhile it seems to me that the facts we have just seen concerning the relative effects of yellow and blue light, may afford a new argument in favour of this supposed relation between the chemical process and the energy of the active rays. In fact we may consider it a limiting case, since it allows us a direct comparison of the relative effects of two groups of absorption bands lying at the opposite ends of the visible spectrum, and consequently possessing the greatest difference possible as to the amount of energy of the corresponding radiations. We have seen that this relative effect was represented by 100 for the

less refrangible part and by only 54 for the more refrangible rays. But we ought to take into account the different degrees of absorption in these two halves of the spectrum. It would seem that the simplest way would be take into consideration the directly visible absorption bands presented by the colouring matter in the same state of concentration as in the leaf (we shall see later how such solutions may be obtained). This was, in fact, the way I first adopted. But this estimate must be considered as not free from error, since the eye is a poor photometer for slight and gradual differences of absorption. This is the reason why in this class of researches, as already mentioned, we must have recourse to the spectro-photometric method.

The choice of the instrument is far from being immaterial—for instance, Vierordt's photometer with a double slit, generally used by German physiologists, is not to be trusted. As the most practical form I consider d'Arsonval's spectro-photometer as furnished by M. Pellin. Here are, for instance, two photometrical curves for solutions of normal and modified chlorophyll of equal concentration. And here (fig. 6A) we have the spectro-photometric curve corresponding to the absorption of light by a single leaf of maple, such as was used for the experiments with yellow and blue light. Reduced to the normal energy spectrum the relative amounts of absorption are measured by the areas *a*, *b*, *c*, *d*, *e*, and *e*, *d*, *f*, *g*, *h*. The total amount of energy of the spectrum I take from Mr. Langley's paper on "Energy and Vision" in the 'Philosophical Magazine' for 1889. The relative values of the energy absorbed by the leaf, as represented by these areas *a*, *b*, *c*, *d*, *e* and *e*, *d*, *f*, *g*, *h*, will be 100 for the yellow and 70 for the blue (fig. 6, B). If plotted together with the previous analytical data (100 and 54) the results of these calculations furnish a new argument in favour of the supposition that the chemical process stands in direct relation to the energy of the radiation.

All things considered, it seems to me that there is a certain amount of evidence for admitting that, so far at least as chlorophyll is concerned, the photo-chemical effect of a radiation depends not only on the degree of its absorption, but at the same time on its energy or amplitude of vibrations; or, to put it in other words, that of two rays equally absorbed, the one possessing the greater amplitude of vibration will produce the greater effect. From this point of view chlorophyll, since of all radiations it absorbs those possessing the greatest energy, may be considered not only a sensitiser but perhaps the best of sensitisers, specially adapted to its function.

I feel that I cannot dismiss the subject without a word of remark concerning the attitude taken towards my researches by the German physiological school, as represented by Julius Sachs and Professor Pfeffer. The latest opinion on the subject expressed by Sachs was the following:—"Alle direkte Beobachtungen zeigen, dass das Maximum

der Sauerstoffabscheidung im gelben Licht stattfindet. Alles zusammengefasst, haben die Untersuchungen über das Chlorophyllspectrum bisher auch nicht die geringste physiologisch werthvolle Thatsache ergeben, d. h. wir würden von der physiologischen Function des Chlorophylls genau dasselbe wissen, wenn uns auch das Spectrum desselben vollständig unbekannt wäre."

It is also a well-known fact that for a long while Professor Pfeffer was my opponent and the staunchest adherent of the old theory. In the first edition of his Handbook he treated my researches in general as an experimental blunder not worthy of further notice. But shortly after the publication of his work a sudden change of scientific opinion was observed in favour of my point of view, thanks to M. Van Tieghem in France, and to Professor Sydney Vines in this country. At the same time Engelmann and Reinke—though using methods far less exact than those I had used—obtained the same results. It was impossible for Professor Pfeffer to hold his position any longer, and in the second edition of his book he practically adopts my views; but this time the conclusions, which were subject to doubt so long as they were associated with my name, are simply attributed to the two German investigators. More than that, a new theory is advanced in order to conciliate his former and present points of view. Professor Pfeffer admits the existence of two different assimilation curves: the one corresponding to the chlorophyll absorption spectrum—the primary as he calls it, and another, the secondary, having its maximum in the yellow rays. But nothing can be more easy than to prove the non-existence of this latter. In fact, if Professor Pfeffer is right, I ought to have obtained his secondary curve. But, as we have seen, I was the first to obtain the primary—the only real one—and that is probably the chief reason why Professor Pfeffer was obliged to pass over my researches in silence. His secondary curve is brought forward in order to cover a retreat imposed on him by the evidence of facts.

Having thus stated the position taken towards me, with rare exceptions, by the German botanists, I feel that I am the more bound to express my gratitude to the late Edmond Becquerel and M. Berthelot, to whom I am indebted for the appearance of my researches in the pages of the 'Comptes Rendus' and the 'Annales de Chimie et de Physique.'

Up to this point we have been considering the qualitative aspect of the problem, we have studied the photolysis or the reduction of the carbon dioxide and the photosynthesis or the production of starch, in their relation to the chemical and optical properties of chlorophyll and to the energy of the active rays. We will now consider the same phenomenon in its quantitative relation to the total amount of radiant energy incident on the green leaf, and we will try to find the law which regulates its dependence on the intensity of the radiation.

Edmond Becquerel, in his already cited work 'La Lumière, ses Causes et ses Effets,' was the first to attack the question of the storage of the solar energy in the green plant; he made the first attempt to obtain an approximate value for what Mr. Horace Brown has recently so appropriately called *the economic coefficient* of the photo-chemical process. Edmond Becquerel arrived at a very moderate estimate. The potential energy represented by the organic matter of a culture of sunflower is only  $4/1000$  of the available solar energy; in a forest it does not surpass  $1/1000$ . A couple of years later, in 1871, I applied the same calculation to more definite physiological data and obtained about 1 per cent. In 1876 my friend Professor N. Müller made for the first time a direct experiment, the leaf which decomposes the carbon dioxide and the pyrheliometer being placed side by side. His estimate is perhaps somewhat too high, being 5 per cent., which I think must be attributed to the fact that the pyrheliometric data seemed to be too low, when compared with the numbers generally accepted. In 1894 I repeated the same experiment by placing the leaf and the pyrheliometer in exactly the same conditions, as will be presently described, and obtained the value  $3\frac{1}{2}$  per cent. It must be noted that in Müller's and my experiments the leaves were placed in an artificial medium, in a gaseous mixture containing from 5—10 per cent. of carbonic acid gas, this mixture giving the highest effect. Mr. Horace Brown has more recently made a highly interesting and much more difficult determination of the same value, placing himself in more natural conditions by using a current of atmospheric air with its normal content of carbon dioxide. The result was 0.5 per cent., but in one case (in which the air had been enriched with carbon dioxide to the extent of about 5.5 times the normal amount) the efficiency of the leaf was raised from 0.5—2.0 per cent.

Now that we are quite sure that only those rays that are absorbed by chlorophyll effect the reduction of the carbon dioxide, it is evident that this economic coefficient must principally depend on the degree of absorption of light by the green matter of the leaf. It is useless to insist how important it is to know this fraction of the total radiation available to the plant. The following thermoscopic method which I adopted in 1884 seems to me still the surest and simplest way of estimating this quantity. The problem, as it presents itself in a real leaf, is highly complicated, because of the scattering effect of the cells and chloroplasts, very similar to that presented by the silver deposit in the photographic plate so ingeniously explained by Sir William Abney. But the problem may be considerably simplified, if for a real leaf we substitute what may be called a liquid leaf.

If using a steel punch we cut out of a leaf a certain area and dissolve its green matter in a volume of alcohol just sufficient to fill a glass cell of exactly the same vertical section, we obtain a liquid

layer of the colouring matter of practically the same concentration. If the absorption due to the glass and to the solvent be determined at the same time, the difference of the two quantities will give us the amount of absorption attributable to the colouring matter of the leaf. All the measurements were made by means of a particular form of thermopile devised by me in 1870 and somewhat like the one recently adopted by Rubens. The bars of the two metals are soldered in a zig-zag, so that the two rows of junctions are turned to the same side. When one row is exposed to the sunlight, the other being sheltered by a screen, we measure the effect of the direct radiation. On interposing the chlorophyll solution we ascertain the fraction of sunlight that is filtered by the solution, and lastly, by interposing the same glass cell with the solvent we find the quantity transmitted by both these media. The difference of these two last quantities corresponds to the absorption by chlorophyll. The ratio of this quantity to the one obtained in the first operation gives the fraction of direct sunlight absorbed by the chlorophyll of a leaf. These three operations may be reduced to two—the measurement of the direct radiation and that of the difference of the two liquids in a double-glass cell. Here is the apparatus arranged for me by M. Pellin in 1889 (Plate 21, A, B).

At the bottom of the cylindrical mantle lies the thermopile, protected by a whole range of double slits from sudden variations of temperature, such as might be caused by wind (Plate 21, A). The double-glass cell, enclosed in a metallic box furnished with two shutters, slides in a groove in front of the outer slits (Plate 21, B). When we perform the first operation, one of the slits is shut by the metallic box (both shutters, of course, being also shut); when performing the second operation the box is made to slide so as to shut both the slits, the shutters being open.

I proposed to call this apparatus a *Phytotetrimeter*, since it gives us the direct measure of the fraction of solar energy available to the plant in the most important of its functions.\* Here are some of the values for a single leaf and for three leaves. Three is the maximum number of leaves that may be superimposed with any profit to the plant, the light reaching the fourth leaf being, as has been proved by Professor Müller, already deprived of its chemical activity.

\* This simple thermoscopic method is in most cases preferable to the far more troublesome method of spectrophotometry.

## Absorption of Solar Energy by the Chlorophyll of Leaves.

## Direct Sunlight.

|                                                           |              |
|-----------------------------------------------------------|--------------|
| Maple, 1 leaf (mean of 32 expts.).....                    | 27 per cent. |
| „ 3 leaves ( „ 4 „ ) .....                                | 31 „         |
| Lime, 1 leaf (mean of 6 expts.).....                      | 29 „         |
| „ 3 leaves ( „ 3 „ ) .....                                | 35 „         |
| Oak, 1 leaf (mean of 4 expts.) .....                      | 23.5 „       |
| Plantain, 1 leaf .....                                    | 23.4 „       |
| <i>Potamogeton lucens</i> , 1 leaf (mean of 8 expts.) ... | 20 „         |

## Yellow Light.

|                                        |        |
|----------------------------------------|--------|
| Maple, 1 leaf (mean of 8 expts.) ..... | 13.8 „ |
|----------------------------------------|--------|

## Red Light.

|                     |      |
|---------------------|------|
| Maple, 1 leaf ..... | 10 „ |
|---------------------|------|

Before applying these values to a full discussion of the question of the economic coefficient and maximum chemical efficiency, the second of the problems we have just stated—the influence of the intensity of light—must be studied. It is too often admitted that the photochemical effect stands in direct proportion to the light intensity, though the contrary has been put beyond any doubt in some cases where most exact methods have been applied. I have but to mention the masterly researches of Sir William Abney on photographic plates.

The influence of the light-intensity on the reduction of carbonic dioxide has been studied by Wolkoff, Van Tieghem, Kreussler, Famin-tzin, and Reinke, but the results being very discordant and difficult to reconcile, I undertook a somewhat detailed study of the question. The methods adopted were the following (fig. 9). In a dark room a pencil of light was obtained by means of a powerful Foucault heliostat (the mirror measuring 18 cm. by 40 cm.) and a lens 25 cm. in diameter. Parallel to the axis of this cone of light was placed an optical bench 2 mm. in length with a scale divided in centimetres, and furnished with five movable and adjustable oblong stands placed across the bench. On each of these stands was placed one of those apparatus with pieces of leaves already described. The distances on the bench were so chosen that the relative intensities of light corresponded to the numbers 1,  $\frac{1}{2}$ ,  $\frac{1}{4}$ ,  $\frac{1}{8}$ ,  $\frac{1}{16}$ , the unit being direct sunlight 3 or 4 hours on each side of noon, when the variation of intensity (as may be seen in the adjoining diagram, borrowed from Crova) is not very considerable. Any experiment, thanks to the gasometric method already described, did not last more than 20 minutes, so that one could be sure of disposing of continual sunshine.



This disposition being rather troublesome, as it implies the use of a dark room and of such expensive and cumbersome apparatus as the large heliostat and the optical bench, I devised later the following more simple and portable form (Plate 22). This time it was the law of the cosines that was applied to measure the intensity of the incident rays. A small metallic platform movable on a vertical axis,

FIG. 9.



and at the same time easily adjustable in the direction of the sunbeam, bears four smaller movable platforms with four glass tubes containing leaves. The four platforms may be put at such angles that the light received by the leaves will vary in the same ratio  $1, \frac{1}{2}, \frac{1}{4}, \frac{1}{8}$  (Plate 22, A). As the experiment lasts only 15—20 minutes, the observer standing by may re-adjust three or four times the position of the large platform, so as to keep the glass tube of the first small platform at right angles with the falling sunbeam. The loss of light due

to reflection and absorption by the glass of the tubes at different angles must be taken into account, and for that reason I prefer using in this case these tubes specially prepared for me at the well-known glass manufactory of Leibold in Köln (Plate 22, B). They are made of plates of mirror-glass luted together. A sample of the same plate is tested photometrically, being placed before a photometer on a divided circle.

The third method was an application of my micro-eudiometer to the measurement and analysis of the bubbles of gas given off by an aquatic plant, a *Potamogeton* or *Elodea*. The quantity of gas produced in 1 minute is sufficient for one analysis, so that the same plant in the course of 10 or 12 minutes may be placed in the different points of the cone of light. Of course this method does not aspire to the same degree of precision as the two former, but its defects are but a consequence of the aquatic habits of life of the plant. On the other hand, it has the great advantage of being applied to the same object, all individual differences being eliminated, and the interval of time being so short that one may be sure of the intensity of light remaining invariable during the four consecutive operations.

On the whole, the results obtained by these different methods on different plants at different times were concordant and may be summed up in the form of the following curve—100 being direct sunshine at about noon, the rays falling perpendicularly on the surface of the leaf (fig. 10).

1. If the whole range of intensities is taken into account direct proportionality is quite out of the question. We may add that Reinke pushed his experiments still further in the direction of higher intensities. Though he used the old method of counting the bubbles, still for such rough approximations his results may be relied upon. On exposing his plant in a convergent cone of light to intensities amounting to two, four, eight times the intensity of direct sunlight, no corresponding rise of the chemical effect could be observed, the curve remaining parallel to the abscissa.

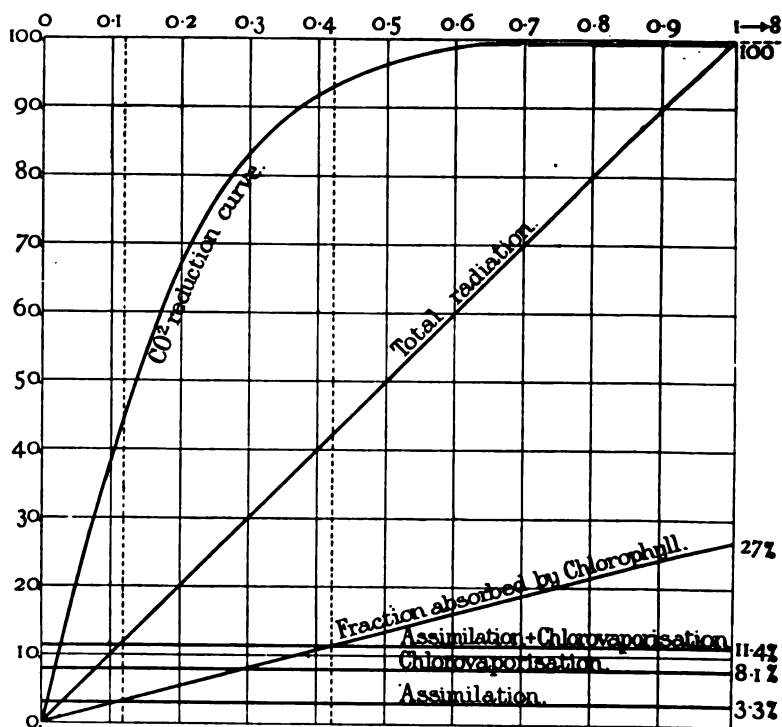
2. The maximum effect is obtained, roughly speaking, at about *one-half* of direct sunlight.

3. Up to a certain degree of intensity the effect may be considered proportional to this intensity. Past a certain point of the curve, for a further rise of intensity there is no corresponding increase of chemical effect.

We must now try to find the reason of this general form of the curve. But before entering on a discussion on this subject, we must first take into consideration one point more, concerning another kind of work produced by the radiant energy absorbed by the chlorophyll of the leaf. Professor Wiesner has put it beyond any doubt that a considerable part of the evaporation going on in the green leaf is accomplished at the expense of the radiant energy absorbed by

chlorophyll. It has since been proposed to denote this part of the process by the special name of chlorovaporisation. My old friend the late Professor Dehérain pointed out a highly interesting fact, subsequently confirmed by Professor Sorauer and especially by M. Jumelle, that these two principal functions of the leaf—the assimilation and the chlorovaporisation—are in a certain sense complementary, the evaporation falling off in the presence of carbon dioxide. This result would seem quite natural, since the same source of energy must be

FIG. 10.



divided between the two processes—had we not known how great is the excess of radiant energy incident on the leaf. But now that we know the available fraction of this total amount, we may try to compare in a rough estimate the quantities of energy absorbed by the leaf with those spent in the chemical work of assimilation as well as in the physical work of chlorovaporisation.

We admitted that the absorption of the chlorophyll of a leaf amounts to 27 per cent. With the diminution of the total energy of the radiation it will fall off in proportion (fig. 10). We have seen further that

the maximum economic coefficient of assimilation in our case was 3.3 per cent. But besides this chemical work there is the physical work of chlorovaporisation going on. In 1894 I made a series of evaluations of the quantities of water evaporated under the same conditions in the same tubes over mercury. Given the conditions of the experiment—evaporation in closed vessels in a saturated atmosphere, one may be sure that the greater part of the process must be attributed to chlorovaporisation.\*

This line here (fig. 10) represents the expenditure of total energy due to chlorovaporisation. It amounts to 8 per cent. This third line represents the sum of work both chemical and physical done in the leaf. It will cross at a certain point the line of available energy and, beginning from this point, the whole available energy would be spent—transformed into work—and consequently the two processes, the chemical and the physical, must interfere as in Dehérain's experiment. Past this point, and of course somewhat earlier, since in no case may the economic coefficient be expected to rise to 100 per cent., the leaf will consequently be short of energy for maintaining both processes at their maximum, and the curve of the chemical process must therefore sink rapidly with the decreasing intensity of the light. At this other point of intersection the whole available energy will not suffice to keep at its maximum the process of assimilation alone. These considerations, it seems to me, give us a sufficient explanation for the first part of the curve.

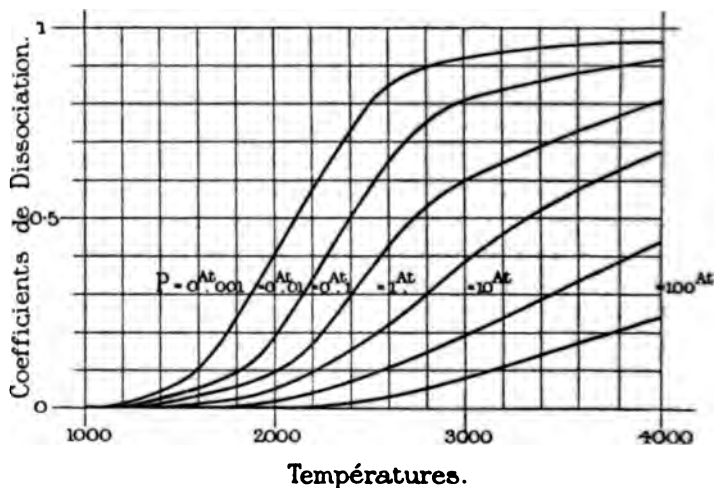
I may add that these results are in full accordance with the beautiful experiments of Mr. Horace Brown and Mr. Escombe. In direct sunshine they found the economic coefficient was but 27 per cent. When the intensity was reduced to about one-tenth, the economic coefficient rose to 95 per cent., nearly the whole being transformed into work.

The next point to be considered, the reason for this form of the upper part of the curve, is somewhat more perplexing. The simplest supposition explaining this course of the process would be to admit that past a certain point the radiant energy incident on the leaf will be in excess. But can it be really admitted that the solar energy may be in excess, remembering always the very modest figure representing the economic coefficient of chemical work?

The chemical process going on in the green leaf is very often considered as somewhat paradoxical. Indeed it takes place at ordinary temperatures, whilst the principal chemical phenomenon which underlies it—the dissociation of carbon dioxide—can be realised in our laboratories only at very high temperatures, amounting to thousands and thousands of degrees. Here is a diagram of Le Chatelier's representing the dissociation of carbon dioxide in its relation to temperature and pressure (fig. 11). But this paradox is of course only apparent, and if

\* I have since made some experiments with variegated leaves of *Aspidistra*.

FIG. 11.

Variation de la dissociation avec  $t$  et  $P$ .

I am not mistaken, it was Count Rumford who showed for the first time that what he called the chemical properties of light may be attributed to its heating power. In his paper "An Enquiry concerning the Chemical Properties that have been attributed to Light" we find the following passage: "The heat generated by the absorption of the rays of light must necessarily at the *moment of its generation* at least, exist in almost infinitely *small spaces*; and consequently it is in bodies that are *inconceivably small* that it can produce *durable effects* in any degree indicative of its extreme intensity." At a still earlier date, in his paper "On the Propagation of Heat in Fluids" Count Rumford even applies this principle of *small spaces*, of the small sphere to which photo-chemical action is restricted, to the case we are now considering. Here are his words: "Will not the admission of our hypothesis respecting the intensity of the heat which is supposed to be generated where light is stopped . . . assist us in accounting for the production of pure air in the beautiful experiments of Dr. Ingenhousz, in which the green leaves of living vegetables are exposed immersed in water to the sun's rays?"

By *small spaces* Count Rumford probably meant molecular spaces, but it seemed to me that it would be highly interesting to test his hypothesis in a rougher way. Now that we are perfectly sure that the phenomenon takes place in the chloroplast, and is due to the rays absorbed, we may try to make a rough estimate of the sphere of action of the sun's rays. The necessary elements of these calculations are the following: the total amount of the radiation as measured by the pyrliometer; the total area of Langley's energy curve; the fraction

of this area corresponding to the absorption spectrum of a single chloroplast, and lastly the thickness of the layer of the colouring matter in this chloroplast.

The total amount of energy is established by Crova's, Langley's, Savelieff's and other researches. I have myself made some evaluations with Crova's portable actinometer. I think we shall be nearest to the truth by adopting the number 1, 3 calories per centimetre per minute.

The fraction of the total energy corresponding to the absorption of the chloroplast was obtained in the following manner. A Sorby-Browning microspectroscope was used without its prism, simply as a colorimeter, in order to obtain a solution possessing the same degree of concentration of the colouring matter as in the chloroplast).<sup>\*</sup> This solution was then studied spectrophotometrically, using d'Arsonval's spectrophotometer in the way already described.

Concerning the last point—the thickness of the layer of colouring matter—I fear I shall be somewhat at variance with the current ideas adopted by histologists. It is generally admitted that the green colouring matter is distributed through the whole body of the protoplast, but many years ago Nägeli, using the following very simple expedient, proved that it is restricted to its surface. If water be added to a preparation (Nägeli used chlorophyll grains of *Clivia* and *Aspidistra*), the chloroplasts burst, and we may see that the green shell or film has for the greater part the appearance of two valves. I have many times repeated Nägeli's experiment with the chloroplasts of *Phajus*, which are far more convenient, being much larger. The chloroplasts liberated from their cells are examined in a solution of sugar, where their appearance is not in the least altered. On the solution being diluted with water, at a certain moment they burst. Adding some sulphate of copper we arrest the process, and obtain durable preparations that may be dyed with Eosine and then present a very elegant object, somewhat recalling the bud of a pink poppy with its bivalved calix.

Another way of testing the distribution of the colouring matter is to inspect the chloroplasts in red light; we may then see the so-called *grana* as very small black specks in a very thin layer restricted to the surface. If we try to estimate the thickness of this green layer or film—a strict measurement is out of the question—we arrive at the approximate value of  $\frac{1}{10}$  of a micron.

Having obtained all these necessary data, we may arrive at our rough estimate of the temperature that could be realised in a minute in this layer of chlorophyll, admitting, of course, that the whole energy would be accumulated without being re-radiated. We arrive at the astounding figure of about 6,000 degrees.

<sup>\*</sup> In actual fact this concentration was reduced to one-half—the reason for this reduction will be seen hereafter, when the structure of the chloroplast is discussed.

I know by my own experience that it is rather difficult to admit such formidable figures. But some analogies may perhaps help us in this respect. If we strike a flint with a bit of steel in a direction normal to its surface we obtain but a very moderate elevation of temperature, but if we hit it in the right tangential direction, so as to concentrate the whole expended energy on a small particle, it is easily brought to incandescence. Or adopting an analogy much nearer to our case; with a condensing lens we obtain temperatures amounting to thousands of degrees\* by increasing the effect in a plane vertical to the falling rays. But we may arrive at the same result by a condensation of the effect in the direction of the falling ray, by diminishing the thickness of the absorbing layer. It has indeed been calculated that a platinum foil not thicker than 1/500 of a millimetre, might be made to melt on being exposed to sunlight, the effect of re-radiation, of course, being eliminated. Practically the reduction of the thickness of the absorbent metallic parts is the plan adopted for augmenting the sensibility in all modern thermoscopic apparatus—the bolometer, the thermopile of Rubens and others. I suspect that it was also the plan adopted by the plant, so that we have one occasion more to repeat with Mr. Horace Brown that the plant seems to know more about physics than we are ready to admit.

Of course these high temperatures, as such, are out of the question, and if I dwell on the corresponding thermometric equivalent of radiant energy accumulated in so small a space and in so short a time, it is only in order to show the analogy with the dissociation process so well studied by chemists. In reality we probably have here the converse of what Wiedemann calls *chemi-luminescence*, that is a direct transformation of radiant energy into chemical work without the transient intermediate stage of a high temperature. In this way the cumulative or integrating effect so characteristic of the photo-chemical process is easily understood. When the carbon dioxide is absent, the radiant energy which can no longer be directly transformed into chemical work is used as heat in the process of chlorovaporisation.

Returning to our curve, which represents the connection between the intensity of light and the quantities of carbon dioxide dissociated in the leaf (fig. 10), and comparing it now with Le Chatelier's dissociation curves (fig. 11), we may perhaps admit that their likeness, which cannot fail to strike one, might be attributed to the same cause—that about a certain point where the curve takes a horizontal direction, the temperature in the chlorophyll film—if I may be allowed, for the sake of analogy, once more to use this term—that the intensity of the radiation accumulated in this small space, is so high that the dissociation of carbon dioxide will be complete. As a consequence, past this

\* My colleague, Professor Zserassky, has obtained in this way temperatures amounting to thousands of degrees.

point any further increase of intensity will be of no avail and the curve must remain parallel to the abscissa.

Of course, I do not pretend that the two values are strictly concordant, but still I think that they are of the same order of magnitude. At all events in this thin film of chlorophyll where an effect corresponding to a very high temperature may be realised, the surrounding space remaining cold, the molecules of the carbon dioxide must be in a state most favourable for their dissociation, resembling very much that furnished by St. Claire Deville's classical *tube chaud et froid*.

These considerations on the extreme tenuity of the chlorophyll film lead to other conclusions the importance of which cannot be exaggerated. For the first time we get an approximate idea of the state of concentration of the colouring matter in the chloroplast. If we take for a unit the concentration of a solution presenting in a sheet of 1 cm. the typical emerald-green colour and the characteristic absorption spectrum, we arrive at the somewhat unexpected result that the concentration in the natural state in the chloroplast is about four thousand times greater. Practically it is very near the solid state, and the superficial colour is nearly black. Two very important conclusions may be inferred from this fact. The first is an explanation of the total absence or very small degree of fluorescence observed in the living green organs. In a very elaborate paper Walter has amply proved that the fluorescence decreases rapidly when the concentration increases. If we take into consideration the state of concentration of chlorophyll in the chloroplast, we may easily account for this absence of fluorescence in the green organs, and at the same time we must admit that the chemical process going on in the chlorophyll molecule must be more energetic when the loss of energy due to fluorescence is at its minimum. For it is a fact, that those chlorophyll solutions which present the least fluorescence are most easily bleached on being exposed to light.

The second conclusion is perhaps of still greater importance. It has been very often repeated that chlorophyll extracted from a living plant loses its power of reducing carbon dioxide, and direct experiments are brought forward in support, in which chlorophyll solutions were put into contact with carbon dioxide and exposed to sunlight without any effect. Now we may see that the results of all these experiments cannot be looked upon as a proof, the conditions being utterly different from those in the chloroplast. The case is just as if we were to measure the absorption of light by lamp-black, and instead of using a coating of pure lamp-black we used a mixture of one part of black and 4000 parts of oxide of zinc. Chlorophyll, as we have seen, is practically black, and if we call it green, it is somewhat in the same sense in which we might call lamp-black brown, for in extremely thin sheets it is of that colour. In the solutions employed till now the



same amount of energy, which in the chloroplast is concentrated in a thin film, was distributed in a mass of liquid thousands of times that thickness. I do not mean that an experiment with chlorophyll in a state of high concentration ought to give a positive result—but it might; the experiment is worth making, and at all events the reverse is not proven. At least I do not see any reason why chlorophyll should act as a sensitiser on AgCl and AgBr, but lose its sensitising power over CO<sub>2</sub>. The difference is only quantitative, not qualitative.

Before dismissing the study of this intensity curve, I should like to mention some applications which it seems to me might be made of this law to certain facts concerning the geographical distribution and some biological peculiarities of plants. It is a well-known fact that in high latitudes plants require less time to arrive at the same stage of development than in lower latitudes. This is generally attributed to the greater length of the summer days. But then the sun does not stand so high in those latitudes, and so long as the chemical effect was considered proportional to the intensity of light, the explanation was evidently unsatisfactory. Now that we know that only about one-half of direct sunlight at noon is utilised, the remaining half being of no use, it is easier to understand that a longer period with a low sun is of greater importance than a shorter period with high sun.

We may take a step further and arrive at the conclusion that the great intensity of the sun's rays at noon may not only be of no use to the plant from the point of view of assimilation, but may become directly injurious, as being the cause of an excessive evaporation, in periods of drought even menacing its existence. Botanists are familiar with many curious peculiarities of structure or habits of leaves, beginning with the pubescence of the upper surface and ending with the vertical position, the rib turned towards the zenith, permanently as in the case of the compass-plant, or periodically as in many cases of diurnal sleep. All these peculiarities are justly considered adaptations reducing to a minimum the amount of evaporation. But one might well suppose that this economy of evaporation could not be realised otherwise than at a proportional loss of assimilation. In order to escape suffering from thirst the plant might be exposed to hunger. Now we may be sure that this is not the case, since about half the direct sunshine at noon is sufficient to maintain nutrition at its maximum. I have plotted (in calories) the diurnal energy curve of Crova, the curve representing the quantity of energy incident on a leaf placed horizontally, and lastly the double curve representing the quantity of energy accessible to a leaf of the compass-plant with its leaves placed in the plane of the meridian, the rib looking upwards. If we remember again that only about half the energy at noon is

available in the process of assimilation, we shall readily see that the difference of these areas for the horizontal and for the vertical leaf will not be considerable, whilst in the latter case the injurious effect of a great excess of radiant energy at high sun, when the saturation of the air is at its minimum, and the evaporation consequently at its maximum, will be spared to the plant. For lower latitudes the result will be still more favourable.

The same considerations hold good when applied to leaves having a woolly appearance on their upper surface, which may be compared to a plate of ground glass. Provided the scattering of light does not diminish its intensity to less than one-half at noon, the plant will be only the gainer in respect of a more economical evaporation, without any injury to its nutrition.

Here I must put a stop to this analysis of the consequences that may be drawn from the study of the optical properties of chlorophyll. It seems to me that all that we know about the function of chlorophyll may be deduced from its optical properties, and this result is quite natural, since the process of assimilation of carbon is at the same time the process of *assimilation of sunlight*.\* The chlorophyll function may be thus considered as the cosmical function of the plant. Professor Boltzman in a remarkable address, read before the Academy of Vienna in 1886, expressed this idea in the following eloquent passage: "Der allgemeine Daseinskampf der Lebewesen ist daher nicht ein Kampf um die Grundstoffe—die Grundstoffe aller Organismen sind in Luft, Wasser und Erdboden im Ueberflusse vorhanden—auch nicht um Energie, welche in Form von Wärme, leider unverwandelbar, in jedem Körper reichlich enthalten ist, sondern ein Kampf um die Entropie, welche durch den Uebergang der Energie von der heissen Sonne zur kalten Erde disponibel wird. Diesen Uebergang möglichst auszunutzen, breiten die Pflanzen die unermessliche Fläche ihrer Blätter aus, und zwingen die Sonnenenergie, in noch unerforschter Weise, ehe sie auf das Temperaturniveau der Erdoberfläche herabsinken, chemische Synthesen auszuführen, von denen man in unseren Laboratorien noch keine Ahnung hat. Die Producte dieser chemischen Küche bilden das Kampfobject für die Thierwelt." From this point of view this field of inquiry on the cosmical function of the green plant is a borderland of two of the greatest generalisations of last century, associated with the names of Lord Kelvin and Charles Darwin—the principle of dissipation of energy and the principle of the struggle for life. And it is with a feeling of veneration that I recollect these words heard many years ago, at Down, from the late Mr. Darwin himself: "Chlorophyll is perhaps the most interesting of organic substances."

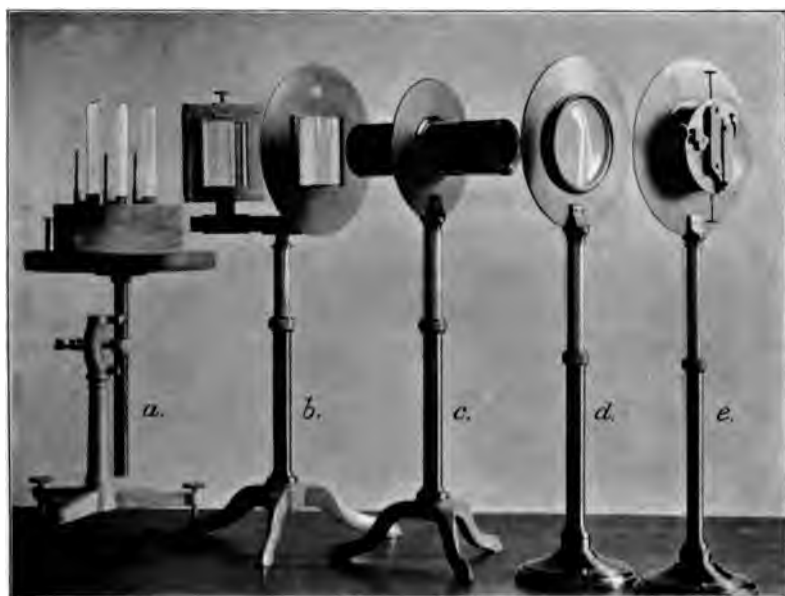
\* "The Assimilation of Light by the Plant" was the original title of my Russian paper on the subject; quite lately I was glad to see this expression employed by Professor Ostwald in his 'Naturphilosophie.'

If we may consider our present notions on the cosmical nature of the process going on in the green plant an outcome of the brilliant achievements of modern physical science, it is only just to try and search for the first pioneers of this important notion of an intimate relation between the vegetable world and the sun, as manifested in the chlorophyll function. Full justice must be done to Senebier for having fully conceived the idea of this wonderful connection. But before arriving at this conclusion we must first give credit to a theory that is too often considered as only a curious aberration of the scientific mind. I mean the theory of Phlogiston. Of course, it was to be expected that a theory that had a Priestley or a Cavendish for its adepts, could not be so easily disposed of, and indeed we know that Helmholtz and especially Professor Odling have made a generous attempt at its rehabilitation. In order to understand the real meaning of this famous theory we have but to substitute for that ill-fated word the more familiar expression of potential energy, and we shall see how near the fundamental conceptions of this phenomenon from the point of view of this theory were to those of our own time, as, for instance, in these words of Senebier: "J'aime voir les corpuscules de la lumière se combiner dans les corps, etc. J'aime à croire qu'ils frapperont de nouveau nos yeux dans la flamme des matières combustibles; il me semble lui voir former les résines avec lesquelles elle a tant d'affinité, les matières huileuses pleines de sa chaleur et de sa clarté, la partie spiritueuse des graines et des fruits, saturée de ses feux. . . Enfin le phlogistique, que la lumière formeroit dans les végétaux, ne seroit-il pas la source de celui qui circuleroit dans les autres règnes?"

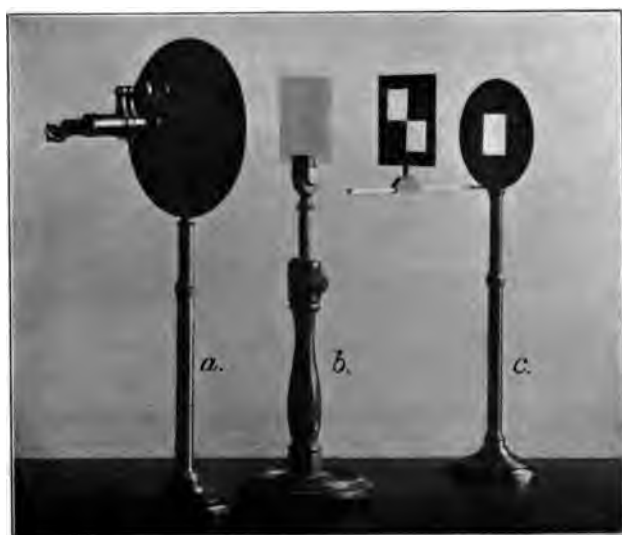
When a botanist on a tour in the botanical garden of Geneva stops to admire the row of marble busts of famous botanists born in Geneva, Senebier in the foreground, he may feel sure that he stands at the very cradle of the physiological research of the 19th century, just as in our days if he would see the place from which will surely spring the physiological movement of the nascent century, he must bend his steps to another botanical garden much nearer to us and salute in the Jodrel Laboratory the starting point of quite a new departure on the way first trodden by Senebier and Saussure.

But in our historical retrospect we must go back another century. Senebier with his characteristic candour mentions the author to whom he was himself indebted for this fundamental notion of an intimate connection between light and matter. We must look for it in a book "written" as the author informs us, "at the desire of some gentlemen of the Royal Society and read at their meetings." We must open the third book of Newton's 'Opticks' and read the 30th question, which runs as follows: "Quest. 30. Are not gross bodies and light convertible into one another, and may not bodies receive much of their activity from the particles of light which enter their composition? For all

**A**

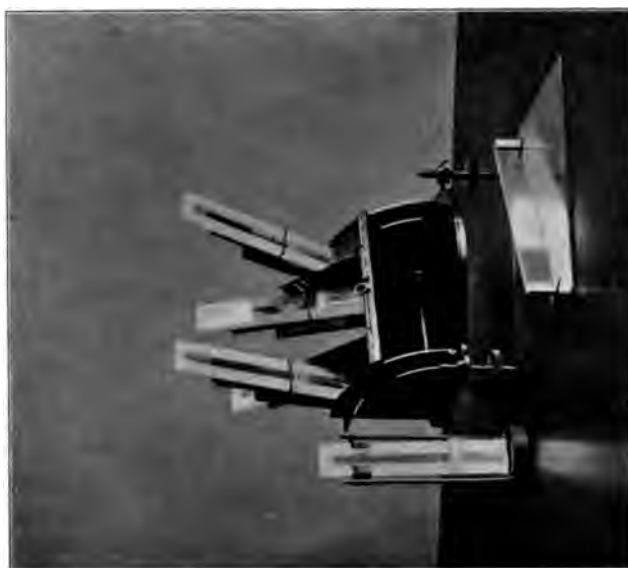


**B**





**B**



**A**





fixed bodies, being heated, emit light so long as they continue sufficiently hot; and light mutually stops in bodies as often as its rays strike upon their parts, as we shewed above." And some lines further: "The changing of bodies into light, and light into bodies, is very conformable to the course of Nature, which seems delighted with transmutations." And further on: "among such various and strange transmutations, why may not Nature change bodies into light and light into bodies?"

If after having read these passages we turn to a micro-spectrum and see the chlorophyll-corpuscles, retaining their natural colour and transparency in the green and yellow rays, turn black as jet on being removed to certain regions in the red and blue, we may be sure, after all that has been said, that here we actually assist at that mysterious "transmutation of light into bodies" which makes of this black speck of matter the real link uniting that glorious outburst of energy in our central star with all the manifold manifestations of life in our planet.

It was the prism which more than two centuries ago revealed the inner nature of the sunbeam. It is the prism again which continues in our President's, in Sir Norman Lockyer's, and other able hands to unravel the mysteries of the origin of this sunbeam, and I am confident that it will still be the prism that will some day fully disclose the ultimate fate of this sunbeam on this our earth: "its transmutation into bodies."

Thus we arrive at the final conclusion that in this book of 'Opticks' we not only find the first and broadest statement of our problem in its actual state, but likewise the surest means towards its probable solution in the future. Little did Jonathan Swift suspect, when writing his envenomed satire on the Royal Society, that that which he took to be the vagaries of a madman was prophetic of Newton's immortal genius.

#### DESCRIPTION OF PLATES.

##### PLATE 20.

Apparatus for experimental research in coloured light of normal intensity (see page 436).

- A. The spectrum is recomposed into two or three vertical bands lying side by side.
- B. The spectrum is recomposed into two bands, superposed one over the other.

##### PLATE 21.

Phytoactinometer—apparatus for estimating the quantity of radiant energy absorbed by the chlorophyll of leaves (see p. 448).

##### PLATE 22.

Cosine photometer, for experimental research (see p. 450).



"On the Nematocysts of *Æolids*." By G. H. GROSVENOR, B.A., New College, Oxford. Communicated by Professor W. F. R. WELDON, F.R.S. Received November 3,—Read November 19, 1903.

While I was at Plymouth in July, 1902, Mr. W. Garstang suggested that I should investigate the origin of the nematocysts found in *Æolids*. He pointed out that no adequate account of their development had been published, and that the view held by some that they were derived from the Coelenterate prey of the *Æolids* had never been properly tested. In looking up the literature of the subject, I came across Strethill Wright's abstract in the 'Microscopical Journal,' mentioned below, which convinced me of the advisability of a thorough examination of the question from this point of view before attempting to work out the development of the nematocysts in the *Æolids* themselves, especially as the few observations I had already made seemed to point in the same direction.

### I. *Historical.*

The cnidophorous sacs at the apices of the cerata of *Æolids* were observed by Linnæus and O. F. Müller. Cuvier and Oken took them for suckers and Nordmann for mucous glands.

Alder and Hancock (1) were the first to observe the expulsion from these sacs of minute elliptical bodies provided with long hair-like tails. They noted a considerable resemblance to spermatozoa, but observed that there is no movement, and no apparent connection with the reproductive system.

These observations were continued by Hancock and Embleton (12), who give an accurate description of the "ovate vesicle," with its external opening and ciliated canal, communicating with the "liver cœcum." They also describe and figure the nematocysts of *E. papillosa*, *E. coronata*, and *E. olivacea*, and their disposition within the "ovate vesicle." They do not commit themselves to a definite opinion, but state that these bodies (the nematocysts) are "more like spermatozoa than anything else"; and they figure spermatozoa from the gonad for comparison, stating that the chief difference between the two are the more rounded body, and altogether inferior size of the latter.

By the time of writing the 'Monograph of British Nudibranchiata,' Alder and Hancock had arrived at a true conception of the nature of these bodies.

In December, 1858, T. Strethill Wright read a paper before the

Royal Physical Society of Edinburgh, in which he maintained that the cnidæ, or thread cells of the *Æolidæ*, were derived from the Hydroids on which they fed. He mentions that the same idea had previously occurred to Huxley and Gosse, and that the latter had suggested the method of proving its correctness. The observations which Wright brings forward in support of this view are as follows:—

1. An *E. nana*, found on a shell covered with Hydractinia, in a pool containing *Campanularia Johnstoni*, had nematocysts of two kinds found in Hydractinia, and also large distinct nematocysts of *C. Johnstoni*.
2. An *E. coronata*, found on *Coryne eximia*, contained nematocysts like those of the latter.
3. An *E. Landsburgii*, found on *Eudendrium rameum*, contained large bean-shaped nematocysts like those of the body of the polyps, and very minute ones, like those of the tentacles.
4. An *E. Drummondii*, found on *Tubularia indivisa*, had nematocysts of four kinds, found in the latter. Having fasted for "a long time," this specimen was fed on *Coryne eximia*. Next morning its papillæ and alimentary canal were crowded with the cnidæ of *Coryne* mixed with those of *Tubularia*.

He remarks that Joshua Alder was unconvinced, on account of the improbability of such a thing being true, and asks for further evidence.

In 1861 R. Bergh published a paper in Danish, which was abstracted in the 'Microscopical Journal,'\* in which he described these organs in several species and genera in which they had not previously been observed. He considers them to be secreted in the cnidosac, and does not mention Strethill Wright's paper.

This omission induced Strethill Wright to publish in the next volume of the same journal an abstract of his former paper, in which he says that further observations and experiments had fully confirmed his view.

Owing either to the absence of figures, or to the afore-mentioned improbability of the conclusions it contained, this abstract seems to have been overlooked as completely as the original paper. I have not found a single reference to it in subsequent literature, and nearly all recent observers have taken for granted that the nematocysts develop within the *Æolidæ* themselves, and several have attempted to work out this development. Bergh has, indeed, mentioned in several places the possibility of a different view; for instance, in a footnote on p. 16 of 'Die Cladohepatischen Nudibranchien,' in reference to the frequent presence of more than one kind of nematocyst in the same individual, he says: "Es ist noch fraglich ob nur eine Art Cnidæ in

\* Vol. 2, 2nd ser.

den Nesselsäcken gebildet wird, und ob die anderen von der Höhle der Leberlappen herrühren, von verzehrten Thieren." On the same page he states that " ganz eigenthümliche, grössere Formen " (of nematocysts) are found in several genera (*Glaucus*, *Coryphella*, *Flabellina*, *Pterocelis*).

Herdman and Clubb (1889), and Herdman (1890), placed beyond doubt, by means of serial sections, the existence of a ciliated canal connecting the cnidosac with the "hepatic" diverticulum. This had, apparently, been doubted by many,\* though I think conclusive evidence on the point may be found in several previous papers by Bergh and Trinchese, not to mention Hancock and Embleton.

In the second paper Herdman states that the cnidosac is "evidently of ectodermal origin." Probably the presence of such typically ectodermal organs as nematocysts was one of the chief reasons of this assertion.

Davenport proved by tracing the actual development that the cnidosac arises not from the ectoderm, but from the distal extremity of the gastric diverticulum. This has since been confirmed by Hecht and Krembrow.

The last four authors have all described and figured what they took to be young stages in the development of the nematocysts, and Hecht and Krembrow have attempted to trace this development in detail. The former considers the nucleus to take a prominent part either by "directing" the secretion of nematocysts by the cytoplasm, or, as he thinks, more probably by giving up a portion of its substance to form the rudiment of the nematocyst. But Krembrow points out that in many cases the cnidoblast is elongated, the nucleus lying at the basal end, while the nematocysts occur from the first at the end next the lumen of the cnidosac.

Most of the other observations which I have found bearing on this question are scattered through works dealing with the general anatomy and classification of the group, and will be more conveniently mentioned later on.

Quite recently, however, since a rough draft of the present paper was already written, a note appeared in the Johns Hopkins 'University Circular' by C. O. Glaser, in which the writer brings forward and discusses the view that the nematocysts of *Æolids* are extraneous and derived from their prey. After pointing out that many *Æolids* are found in association with hydroids or actinians, and that Alder and Hancock observed fragments of a hydroid in the alimentary canal of an *Æolid*, he shows that the present accounts of the development of nematocysts are unsatisfactory, and that the appearance of nematocysts in endodermal cells, and apparently independent of the nucleus, is at least unexpected. He then records three observations of his own in support of this view—

\* See Lankester's "Mollusca," 'Encycl. Brit.,' 9th edit.

1. An *E. alba*, found on a colony of *Paripha*, had nematocysts of two kinds, indistinguishable from those of the hydroid.
2. An *E. rufibranchialis*, found on *Eudendrium*, had nematocysts about one-third the size of those of *E. alba*. These were apparently not compared with those of *Eudendrium*; at any rate the result of the comparison is not given.
3. A young *E. alba* was found in a large vessel of sea water in which various marine larvæ were being reared. This *Æolis* must have been over 2 months without hydroid food and had probably metamorphosed in the vessel. It had no nematocysts.

Having discussed one or two difficulties, the writer concludes that further investigation of this point is desirable, and that it may turn out that nematocysts are not "part of the organic make-up" of the *Æolidæ*. He is apparently unaware of Strethill Wright's work.

## II. *The Nematocysts of Æolids are derived from their Cœlenterate Prey.*

Before describing my experiments, which, I think, afford conclusive confirmation of Strethill Wright's view, I shall proceed to discuss a number of facts which have come under my own observation, or which I have collected from the literature of the group, which point in the same direction and would, indeed, be sufficient by themselves to prove the truth of this view.

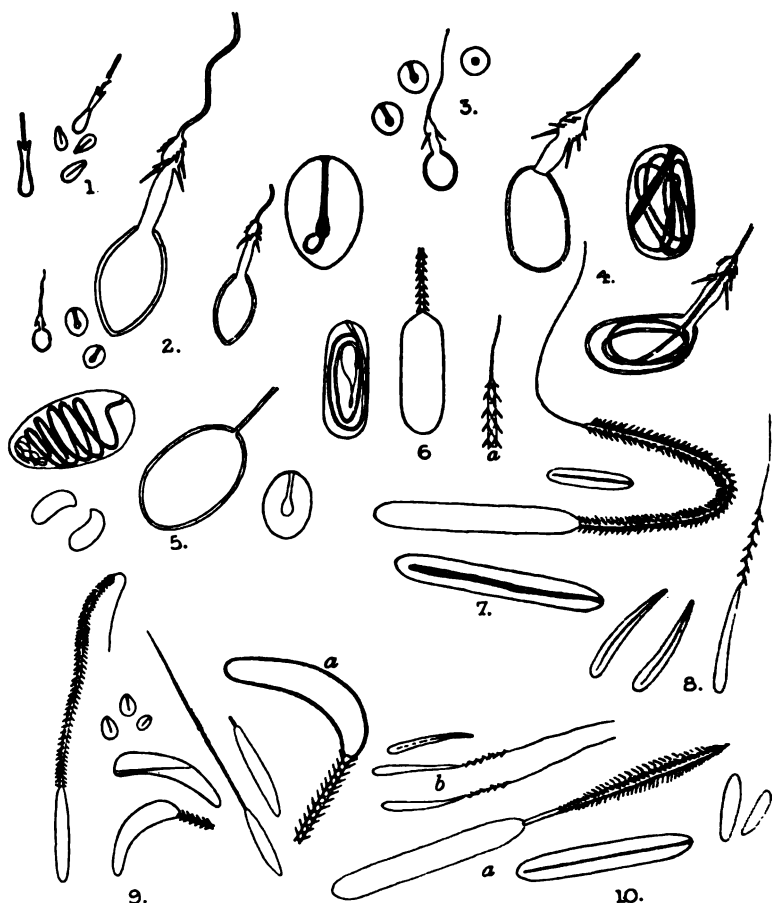
### 1. Great Similarity of the Nematocysts of *Æolidæ* and *Cœlenterates*:

I think that those who quote the nematocysts of Nudibranchs and *Cœlenterates* as a striking example of homoplasy or convergence, can scarcely be aware of the astonishing completeness of this assumed convergence. It is not simply a case of nematocysts of the same general plan occurring in the two groups, but of each of several distinct forms of nematocysts being found in both groups. For instance, the most characteristic Actinian nematocysts have elongated semi-cylindrical capsules; they are either straight, varying from 20—60  $\mu$  in length, with the basal portion of the thread (twice the length of the capsule) thick, and closely covered with long fine bristles (fig. 7); or the capsule is slightly curved, about 25  $\mu$  in length, and narrower in proportion than in the last form, while the thread is uniformly tapering, slightly spiral, and furnished with short relatively stout barbs for a distance rather less than the length of the capsule (fig. 8). Both these forms are of frequent occurrence in *Æolids* belonging to Bergh's sub-family *Æolidiade propriæ*.

Small nematocysts, 8  $\mu$  or less in length, shaped something like an apple pip (fig. 1), are very widespread in the hydroidæ; they occur,

with slight variations in actual size and in relative breadth, in *Eudendrium*, *Gonothyrea*, *Obelia*, *Sertularia*, *Sertularella*, *Antennularia*, *Plumularia*, &c.; they are also, perhaps, the most common form in *Æolids*, as may be seen from a glance at the plates in Bergh's "*Beiträge zur Kenntniss der Aeolidiadae*," or Vayssière's "*Opisthobranches du Golfe*

Figs. 1—10.



de Marseille." I myself have found them in the following genera:—*Rizzolia*, *Calma*, *Flabellina*, *Coryphella*, *Amphorina*, *Facelina*, *Galvina*.

Rather small spherical nematocysts, very like those of *Hydra*, are found in *Tubularia* and other marine hydroids. I have found them in *Rizzolia*, *Coryphella*, *Facelina*, and *Cuthona* (fig. 3).

These facts are in no better accord with the idea of genetic relation-

ship,\* for nothing short of the polyphyletic origin of *Æolids* from diverse Coelenterates would bring us any nearer an explanation.

2. Nematocysts of different types occurring in individuals of the same species, or in the same individual.

The following instances will illustrate this:—

- i. Of 48 *R. peregrina*, while all had small pyriform nematocysts (fig. 1),
  - (a) 20 had no others,
  - (b) 16 had also large bean-shaped nematocysts, like those of *Eudendrium* (fig. 4),
  - (c) 10 had both these, and also small round *Tubularia*-like nematocysts (fig. 3),
  - (d) 1 had only small pyriform and small round nematocysts,
  - (e) 1 all the forms found in (c), and in addition a few similar to those shown in fig. 6, but about half the size.
- ii. Of 29 specimens of *Spurilla neapolitana*, 26 (including 4 young specimens from 1·5—2 cm. long) had nematocysts shown in fig. 8; three very young specimens (less than 1 cm. long.) had nematocysts like those in fig. 9. This may, perhaps, indicate that a change of food is a regular occurrence in the life-history of this species.
- iii. Of two young specimens of *Facelina punctata*, one had nematocysts of at least five different kinds, shown in figs. 1, 3 and 5; the other had nematocysts of two kinds indistinguishable from those of *Pennaria Cavolinii* (see below), (fig. 2).

Such individual variations have often been noticed by writers on this group, and in his recent paper on the development of the cerata, Krembrow remarks on such a case in *Æolidiella glauca*, one of his specimens having a different type of nematocysts from the others; he seems almost inclined to consider it a different species on this account, though after a careful examination he was unable to discover any other difference, anatomical or histological.

I imagine that what uniformity in this respect does exist (and this must be considerable in the majority of species, or the idea of the development of nematocysts within the *Æolids* would never have endured so long), must be due to a decided preference on the part of each species of *Æolid* for a particular kind of hydroid, for living and feeding on which they are specially adapted. In this connection the case of *Flabellina affinis* and *Coryphella Lansburgii* is interesting. These species are by no means nearly related, being placed by Bergh in separate sub-families. But in external appearance they show a remarkable resemblance. The specimens I have examined show

\* *Vide* Lankester's 'Treatise of Zoology,' Part IV, p. 12.

approximately the same range of variation in size; the colour in both is a beautiful translucent violet, with brick-red or carmine diverticula of the gastric gland showing through the integuments of the cerata. I have no direct evidence as to what hydroids they frequent, but I have on several occasions received specimens of the two species together, and the evidence of their nematocysts given in the following table, leaves no doubt that their food is the same. This is probably, therefore, a case of mutual mimicry, since both species are protected (by mucous glands and nematocysts).

|                                  | Small pyriform nematocysts and large bean-shaped nematocysts of Eudendrium. | Small pyriform and large oblong nematocyst (fig. 6). | All three kinds. | Total. |
|----------------------------------|-----------------------------------------------------------------------------|------------------------------------------------------|------------------|--------|
| <i>Flabellina affinis</i> .....  | 2                                                                           | 4                                                    | 2                | 8      |
| <i>Coryphella Landsburgii</i> .. | 3                                                                           | 4                                                    | 2                | 9      |

The nematocysts figured in fig. 6 I have not as yet been able to find in any Cœlenterate; they are apparently those which Bergh considers "ganz eigenthümliche." But I think the evidence is scarcely in favour of this view, even when this case is considered by itself. For, as shown above, these nematocysts are found in about half of each of these by no means nearly related species; while, on the other hand, I could not find a trace of them in two specimens of *Cor. Scarchiana* or five *Cor. lineata*. I have not had an opportunity of examining any other species of *Flabellina*.

3. Whenever it is known what particular Cœlenterate an *Æolid* has been feeding on, the nematocysts of the two are found to be identical.

Strethill Wright gave four instances of this and Glaser has given another. I may add a few more.

As mentioned above, the *Æolidiadae propriae* of Bergh have usually typical Actinian nematocysts, and many of them are known to feed on Actinians. An *Æe. papillosa* found at Plymouth among stones on which the common red Anemone was abundant, had nematocysts indistinguishable from the latter. An *Æolidiella Alderi* dredged at Plymouth had nematocysts exactly like those of *Sagartia* (fig. 6). It is known to feed on a species of *Sagartia* (see Garstang (9)). Mr. Garstang told me that he had been struck by the similarity of the nematocysts of these two animals some years ago, and showed me drawings he had made at the time.

Also two *Amphorina cerulea* found on *Sertularella*; a *Facelina* sp. found on *Antennularia*; a *Cuthona aurantiaca* and three *Facelina coronata* on *Tubularia*; *Facelina punctata* on *Pennaria Cavolinii*; three *Rizzolia peregrina* dredged with *Eudendrium rameum*; four *Rizzolia peregrina* dredged with *Eudendrium* sp.; all had nematocysts indistinguishable from those of the hydroid with or on which they were found.

But it is possible in many cases where the "food hydroid" of an *Æolid* is unknown, to prove that the nematocysts in the cnidosacs of the *Æolid* are the same as those of its prey, whatever that prey may be; for it has been noted by several observers (Alder and Hancock, Hecht, &c.) that the fæces of *Æolids* consist largely of nematocysts, obviously derived from their food, but no one seems to have compared them with those found in the cnidosacs. I have made this comparison in a number of cases, and have always found the nematocysts in the fæces identical with one or more forms which occur in the cnidosac. In those individuals which have many different types of nematocysts in their cnidosac, these are not always all represented in the fæces, for the latter are extruded a day or two at most after the meal of which they are the remains, while nematocysts may remain in the cnidosacs for at least a month, as is proved by an experiment to be described presently.

4. Those *Æolids* which are known to feed on animals unprovided with nematocysts have no nematocysts themselves:

Thus the sub-family Janidæ, many of which are known to feed on Polyzoa (see Garstang (9) and Giard (10)), have no nematocysts. Since these forms have also no cnidophores and in many other ways are very aberrant, it might be objected that they branched off from the *Æolid* stem before the acquisition of nematocysts by the latter, and the fact of their feeding on Polyzoa was a mere "coincidence." This objection, however, cannot apply to the case of *Calma glaucoides*. This is in all other respects a typical *Æolid*, but, according to M. Hecht (1), it has no nematocyst and no cnidosacs. According to the same author there can be no doubt that the food of this species consists of the eggs and embryos of various shore fish (Cotta, &c.). The only other member of the genus *Calma* is *C. Cavolinii*, which has typical cnidophores, usually crowded with nematocysts, and which feeds on hydroids, for I have found unmistakable fragments of the same in the stomachs of several specimens, as well as nematocysts in the fæces.

M. Hecht, seeking an interpretation of the coincidence of non-coelenterate food and absence of nematocysts in *C. glaucoides*, in the light of the current opinion as to the origin of nematocysts in Nudi-branches, writes as follows: "On peut considérer l'absence de sacs à nematocystes chez *C. glaucoides* comme un pur phénomène de dégénérescence, étant donné qu'ils existent chez une espèce voisine; quant à



la cause, elle est difficile à pénétrer. On sait que les *Æolidiens* se nourrissent fréquemment de *Cœlentérés* (*Hydraires*, *Actinies*), et paraissent doués d'immunité vis-à-vis de leur *nématocystes*; or il est curieux de se remarquer que c'est précisément une espèce qui ne s'attaque pas à des *Cœlentérés*, qui est dépourvue de sacs *cnidophores*."

We see from this case that the degeneration and atrophy of the *cnidosacs* follows very soon the abandonment of a *Cœlenterate* diet.

*Fiona* is another genus unprovided with *cnidosacs*. I have not been able to find any record of the food of this genus, but Dr. Lo Bianco tells me that about 3 years ago large numbers of *Fiona nobilis*, *Velella* and *Janthina*, were taken together in the Bay of Naples, and that he observed the *Fionæ* feeding on *Velella*, the individuals which had so fed being coloured a deep blue. *Velella* and *Fiona* were also taken this spring in company, and I observed *Fiona* devouring the *siphonophore*; a normally coloured *Fiona* becomes blue very soon after feeding on *Velella* and its gastric diverticula become crowded with *nematocysts*. The blue colour persists for a considerable time (a week to 10 days) without a further supply of *Velella*, so that if this was the staple food of this species, we should expect the majority to be blue, which is not the case. Besides those taken with *Velella*, a number of *Fiona nobilis* were found on floating pieces of pumice or wood covered with a species of *Lepas*. I kept one such colony in a large jar of sea-water, and next morning the bodies of half-a-dozen barnacles were lying on the bottom, their stalks having disappeared. As the remaining barnacles were quite healthy, I think there can be no doubt that the stalks had been devoured by the *Nudibranchs*. It seems probable, therefore, that the food of *Fiona* is varied, and that the proportion of *Cœlenterates* is not sufficient to give a constant supply of *nematocysts*, so that the *cnidosacs* have been lost or never developed.

5. The inadequacy of the published accounts of the development of *nematocysts* in *Æolids* is remarked on by Glaser, who also points out that even if undoubted developmental stages were found, it would not prove that they arose in the *Æolid*, for they might well be introduced together with the fully formed ones. The comparative scarcity of young stages (I myself have never found anything which I could confidently affirm to be such) I take to be due to the following causes:—

- (1) The development of *nematocysts* in the less accessible basal part of the polyp and their migration only when fully formed to the exposed positions where they are of use.
- (2) The greater digestibility of the young stages. *Spirocysts* must also be digestible, for though they are as numerous as *nematocysts* in many *Actinians*, they are not found in *actinian-eating* *Æolids*. But Bedot states that he has found them in *Pleurophyllidia* (3).

## 6. The Ciliated Canal between the Gastric Diverticula and Cnidosac:—

The existence of this canal, as mentioned above, was first established in transparent pupillæ by Hancock and Embleton, and subsequently by means of serial sections by Herdman and Clubb and others; but its function has always remained a mystery. Hecht suggested that it might act as a safety valve, to allow the escape of superfluous nematocysts from the cnidosac. Krembrow combats this view and maintains that the function of the canal is to allow the passage into the cnidosac of nematocysts developed in the "liver cells." Though there is no better evidence for the development of cnidæ in the "liver" than there is for their development in the cnidosacs, this view is certainly more in accordance with observed facts than the former. For as Hancock and Embleton observe, the cilia on the walls of the canal cause a current towards the cnidosac; these naturalists also note that particles of various sorts, "accidentally pressed into the canal," are carried into the cnidosac. Trinchese (1) actually observed the passage of nematocysts in this way,\* but, like Hancock and Embleton, he considered this a purely artificial effect. He notes that the cnidæ so passing are sometimes like those already in the cnidosac, sometimes different, and remarks: "In ambo i casi esse appartevano ad individui mangiati dal suddetto animale (*Facelina* sp.); nel primo caso esse appartevano a qualche *Facelina*, nel secondo ad *Æolididae* di altri generi." It is curious that he does not consider the possibility of their derivation from Coelenterate prey. I have also observed the passage of nematocysts through the canal, and certainly in this case they belonged to a hydroid (*Pen. Cavolinii*) devoured a short time before.

The ciliated canals and cnidosacs have of course no power of distinguishing nematocysts from other small indigestible bodies. Thus Hecht observed that when some *Facelina coronata* had been feeding on *Elysia*, the radular teeth of the latter appeared in the cnidosacs of the *Facelina*. I have observed the same thing in the case of *F. Drummondii* which had devoured two small specimens of *R. peregrina*. Probably the bâtonnets mentioned by Vayssière as occurring in the cnidosacs of *Flabellina affinis* and other species of *Æolids*,† are due to the individuals in question having varied their diet by devouring some spiculiferous organism.

*Experiments*.—Strethill Wright's most conclusive evidence for the extraneous origin of nematocysts in *Æolidæ* was his experiment of feeding an *E. (Facelina) Drummondii*, having Tubularia nematocysts in its cnidosacs, on *Campanularia Johnstoni*, the nematocysts of which subsequently appeared in the cerata of the *Æolid*. I have carried out similar experiments on a number of individuals of two species of *Æolids*,

\* Part II, p. 53.

† *Loc. cit.*, p. 82.

*Rizzolia peregrina* and *Spurilla neapolitana*, which are the species most easily obtained in the late autumn at Naples.

1. Four specimens of *Rizzolia peregrina* were obtained at the beginning of November, being dredged with some tufts of *Eudendrium*. These had nematocysts of one kind only, which were small (average length  $6.5\ \mu$ ), pyriform or pip-shaped, and are shown in fig. 1. These specimens were placed in a small aquarium with several colonies of *Pennaria Carolinii*. The nematocysts of this hydroid are of two kinds, which differ chiefly in size, the larger being about  $25\ \mu$ , the smaller  $7\ \mu$ , in length. They are oval, and slightly pointed at the end of the capsule opposite the base of thread (fig. 2). It will be seen that these could not possibly be confused with the nematocysts found in the cnidosacs of the *Æolids* at the time of capture.

For some days the Nudibranchs were too much occupied in depositing eggs to pay any attention to the unaccustomed food provided for them, but on the ninth morning I noticed that several branches of the hydroid were denuded of polyps, and, on examining the cerata of the *Æolids*, I found a considerable number of *Pennaria* nematocysts mixed with the original ones, which were still preponderant in numbers.

Remembering Bergh's opinion, that one kind of nematocyst is developed in the cnidosac, while others may be derived from hydroids, I continued to feed these individuals on *P. Carolinii* for a month. At the end of this time the original nematocysts were almost entirely replaced by those of *Pennaria*; in some papillæ I could not find any but the latter, and in none that I examined did the small pyriform cnidæ amount to more than 2 per cent. of the total number in the cnidosac.

2. Four other specimens of *R. peregrina* were kept in an aquarium with *Eudendrium*, *Pennaria*, *Tubularia*, and *Aiptasia variabilis*. These specimens had at capture nematocysts of two kinds found in some species of *Eudendrium*; the small pyriform kind is shown in fig. 1 (occurring on the tentacles of the hydroid), and large bean-shaped ones, shown in fig. 3 (found in a definite zone on the body of the polyp). After a month in the aquarium they had, of course, still a number of *Eudendrium* nematocysts, since this hydroid was included in their food; but they had also a considerable number of *Pennaria* and *Tubularia* nematocysts, and a few from the acontia of *Aiptasia*, though the latter is very different from their accustomed prey, and, in fact, *R. peregrina* does not seem adapted to attack Actinians (see below). Besides these there were a few oval nematocysts, with a considerable length at the base of the thread, covered with fine barbs, which must have been derived from a small hydroid inadvertently introduced with the others, and which I have not been able to identify; they certainly cannot be the nematocysts developed in *R. peregrina*, since they only

occurred in two of these specimens, and in none of the other fifty I have examined.

3. Two specimens of *R. peregrina* were placed in a large jar of sea-water, with two amputated probosces of *Cerebratulus urticans*. They did not take kindly to the diet, but, after several days, one had eaten sufficient to fill its cnidophores with an inextricable tangle of the long sinuous nematocysts of the nemertine, while the other had a few of the same both in the cnidophores and in the "hepatic" diverticula.

4. Two specimens of *Spurilla neapolitana*, which had nematocysts of one sort only shown in fig. 8, were fed on *Aiptasia variabilis*, which has two kinds of nematocysts, shown in fig. 7; the cnidosacs of the *Æolids* soon became crowded with the nematocysts of *Aiptasia* (especially those of the *acontia*), but I was not able to continue the experiment long enough to entirely replace the original form. Besides the two forms of nematocysts mentioned, *Aiptasia* has a large number of small spirocysts. These have a much more fragile appearance than true nematocysts, and they must be destroyed and digested by the gastric fluids of the *Æolids*, for I could not find any in the cnidophores of these two specimens.

In all these cases the nematocysts newly introduced did not simply lie free in the lumen of the cnidosac, but were included in "cnidoblasts" in the same way as those present in the *Æolids* at capture (fig. 12).

### III. Function of Nematocysts and Cnidophores of *Æolids*.

If it is allowed that the nematocysts found in the cnidosacs of *Æolids* are of extraneous origin, and, in fact, are *quasi* fecal products of the digestion of coelenterate prey, the question arises, "Is the elimination of these inconvenient, and possibly dangerous constituents of the food, the sole function of the cnidosacs and their associated mechanism, or do they also serve as a means of offence or defence"? The difficulty of believing that the *Æolid* uses for its own purposes the very weapons presumably "intended" to defend the hydroid from the *Æolid* and other enemies, seems to have been the chief cause of Alder's scepticism in regard to Strethill Wright's results. The nearest parallel I know of is the case of the Cephalopod *Tremoctopus microstoma*, described by Troschel, and later by Joubin, as possessing nematocysts borne on special cylinders on the arm. M. Bedot has proved by sections that these cylinders are nothing more nor less than fragments of the arms of a Medusa, and he remarks: "Nous avons, donc, ici un exemple intéressant d'un animal empruntant pour sa défense les armes d'un autre animal, caractère considéré habituellement comme étant l'apanage exclusif de l'homme." In this case, however, direct evidence of the use of the nematocysts seems entirely wanting, and it is only the regular

occurrence of these cylinders which leads one to suppose they must serve some useful end. Certainly, the evidence of the use by the *Æolids* of their stolen nematocysts is very much stronger.

In the first place, the nematocysts discharge themselves, after extrusion from the cnidosac. I mention this, because the fact might be considered improbable, though it has been recorded by many observers. It is true that, in many cases, the cnidæ are so minute, and the discharge is effected with such rapidity that the act itself is difficult or impossible to follow. But tips of the cerata are so transparent that the cnidæ can usually be seen lying in the walls of the cnidosac undischarged; whereas a second or two after they have been extruded into sea water, the threads of the majority are everted. Sometimes the actual eversion itself can be seen, as when the thread is very conspicuous (*e.g.*, large Actinian nematocysts) or when, for some reason, the eversion takes place slowly. For instance, I have seen the large bean-shaped nematocysts of Eudendrium from a cerata of *R. peregrina* evert the distal portions of their threads with great deliberation; the part already everted lengthened with a curious sinuous motion of the tip, while the part still within the capsule uncoiled itself at a corresponding rate. (I need hardly say that I cannot confirm M. Hecht's opinion that the nematocysts of Nudibranchs differ from those of Cnidaria, in that only the basal portion of the thread of the power is inverted, the distal part being coiled up inside the inverted base; on the contrary, in all cases, in both Nudibranchs and Cnidaria, in which I could clearly distinguish the thread inside the capsule, it was coiled up more or less regularly, between the inverted base and the wall of the capsule, and must, therefore, have been inverted itself.)

The arrangement of the nematocysts within the cnidosac seems to indicate that they are used as weapons, for they usually lie with the aperture, through which the thread will be everted, turned towards the periphery of the "cnidoblast." It is true that the round Tubularia-like nematocysts lie much more indiscriminately, and that even the long Actinian nematocysts are sometimes reversed, but as a general rule the arrangement is as described.

The fact that those species which have no cnidosacs are more richly provided with glands on the cerata, as if in compensation for their absence (see Hecht on *Calma glaucoides* and Krembrow on *Fiona*), seems to point to the same conclusion.

But if the nematocysts are used as weapons, they may be either—

1. Offensive weapons, used against prey,
2. Defensive weapons, used against enemies.

1. This view was suggested by Bergh in his paper of 1861 (according to the abstract in the 'Microscopical Journal'). But I have often watched *Æolids* feeding, and noticed that the cerata are held in the normal

position, directed backwards along the sides of the body; moreover, it is doubtful whether the nematocysts which, in the ordinary course of events, would have been derived from the very species being devoured, would be very effective for paralysing the same.

2. The second alternative is the one most generally accepted, and I think it is undoubtedly the correct one. The experiments of Herdman and of Garstang prove that *Æolids* are unpalatable to many fish (apparently not to all, for McIntosh states that the cod eats *Æolis papillosa*, but according to the same authority the most deadly bait for cod are bright coloured anemones, and young flat fish fill their stomachs with *Edwardsia*; so that for these fish nematocysts evidently have no terrors). No one can have witnessed the reaction of an *Æolid* to various stimuli (touch of a foreign body, agitation of the water or, in some cases, a shadow), without being convinced that the cerata are used as a means of defence. The body is contracted, the head being often nearly telescoped into the trunk, while the cerata are erected and waved about, especially in the direction of the foreign body, and are often considerably extended (in *R. peregrina* the cerata when excited are nearly double their length when at rest).

But though the nematocysts are undoubtedly used defensively, I think the actual method employed is generally misunderstood. The *Æolid* is often described as "threatening" the foreign body with its cerata, the supposition being that nematocysts are shot out against it. It is certainly true, as stated above, that the cerata are turned towards the foreign body which has touched the animal, but in experiments on upwards of 40 individuals I have never seen nematocysts extruded under these circumstances; and the mass of nematocysts extruded from a cnidosac is quite visible to the naked eye. I have, indeed, only once witnessed the emission of nematocysts for cerata still attached to the body of an *Æolid*, and not themselves individually squeezed or otherwise ill-treated. On this occasion a *Sp. neapolitana* about 3.5 cm. in length, in a small beaker of sea-water, was somewhat violently stimulated with a glass tube. It erected its papillæ, which in this species are very numerous and usually carried curled up along the sides of the body, and lashed them about in all directions, at the same time emitting quite conspicuous little masses of nematocysts from its cnidosacs. These were carried by the currents in the water and adhered as a flaky white deposit to the bottom of the vessel. On examination they were found to consist almost entirely of discharged nematocysts. It is, I think exceedingly doubtful whether this promiscuous discharge would have much effect on such an enemy as a fish, for

- (1) A very small proportion of nematocysts would come in contact with the fish,
- (2) Since eversion of the thread follows, as a rule, very rapidly on

the extrusion from the cnidosac, the few that did reach the fish would probably be already discharged,

- (3) It is very doubtful whether nematocysts would penetrate the scaly covering of a fish large enough to be dangerous to an *Æolid*.

It is, therefore, not surprising that this method of defence is not more generally employed.

With this single exception, in all the *Æolids* with which I experimented nematocysts were emitted only when individual cerata were squeezed or plucked off. In this way a fish which had snapped at the cerata, the loss of which, as is well known, does not seem to inconvenience the Nudibranchs at all, would receive a discharge of nematocysts into its mouth, where they would probably act with the greatest possible effect. This is in complete agreement with Garstang's view as to the meaning of certain features in the coloration of *Æolids*. He suggests that the localisation of the bright colours in the cerata "serves to direct the experimental attacks of young and inexperienced enemies to the non-vital papillæ and away from the vital and inconspicuously coloured parts of the body," and "at the same time gives them (the enemies) the needful experience of the unpalatable nature of their intended prey" ((9) p. 175). The erection and elongation of the cerata conduce to the same result (*i.e.*, make them the most probable mouthful for an enemy), even when the bright colours are absent or otherwise disposed.

But though the nematocysts are certainly used as defensive weapons, their removal from the digestive system is an important, perhaps the original, function of the cnidosacs. In molluscs other than the cladohepatic Nudibranchs, the food is digested in the stomach, the liquefied products being passed into the gastric gland, where absorption takes place (see Simroth (20)). In *Tritonia*, therefore, the anus suffices for the passage of nematocysts out of the body. But in the Cladohepatica part of the food is digested in the gastric gland, quite fresh pieces of hydroid being found in the ducts and ceratal diverticula of a recently fed *Æolid*. On examining the cerata of a *Doto* which had been feeding on *Pennaria Carolinii*, I found them crowded with large nematocysts. How Dotonids, which habitually feed on hydroids and have no apertures in their cerata, get rid of the nematocysts I cannot say; perhaps by throwing off their cerata, which as is well known they do with great ease. When an aperture for the extrusion of nematocysts had once been acquired, it would be obviously advantageous that the distal end of the "hepatic" diverticulum should be modified to form a cnidosac where the nematocysts might be stored to be used in defence as required.

IV. *The Mechanism of the Discharge of Nematocysts.*

To understand how an *Æolid* is able to swallow *Cœlenterate* nematocysts undischarged, pass them in this condition through its alimentary canal, and then discharge them in its own defence, we must know something of the conditions and causes of this discharge. As far as I know, this question has never been discussed as regards *Nudibranchs*, but the theories brought forward to explain the action of the nematocysts in *Cœlenterates* are innumerable. In 1887 von Lendenfeld considered the solution of the problem in sight; but ten years later he confesses that the increase of knowledge has only multiplied hypotheses, and an adequate explanation seems further off than ever. I think a consideration of the behaviour of nematocysts in *Æolids* throws some light on the question.

When nematocysts are extruded from a cnidosac and subsequently evert their threads, not only have the original *Cœlenterate* nematocytes been digested, but the nematocysts are often quite free from any trace of protoplasmic substance, even the "cnidoblast" in which it was contained in the cnidosac. The discharge, therefore, cannot be directly due to the contraction of the nematocytes or surrounding tissues of the *Cœlenterate*.

Nussbaum and others have suggested that the elasticity and tension of the capsule itself aids in causing the eversion of thread, while Grenacher considers this tension sufficient in itself to evert the thread but for the resistance of the operculum ("Deckelchen") covering the opening; any slight access of pressure from outside suffices to overcome this resistance and causes the discharge. But in this case the nematocysts would be at least as likely to be discharged while being swallowed by the *Æolid*, as when lying undisturbed in the sea water after extrusion from the cnidosacs.

The theories so far discussed rely on the assertions of H. Frey, Clarke, Gräffe, and others that the capsule of a nematocyst is smaller after than before discharge. Iwanzoff, on the other hand, from a series of measurements and calculations, reaches the conclusion that while the capsule itself may be smaller, the total capacity of the nematocyst is larger after discharge. For in a resting nematocyst the volume of the thread must be subtracted from that of the capsule; while in a discharged nematocyst, the thread being hollow, its capacity must be added to that of the capsule. The substance contained in the capsule has therefore increased in volume, and Iwanzoff considers this to be the cause of the eversion of the thread. He supposes the original contents of the nematocyst to consist of a highly hygroscopic gelatinous substance; this is protected from the access of water by the impervious capsule wall and the operculum over the aperture of the inverted thread. When this operculum is removed by the action of the



nematocytes or other cells, and the nematocyst itself is thrust out into the water, the latter enters the basal portion of the inverted thread, diffuses through its thin walls and causes the gelatinous substance to swell up. He mentions in support of this the staining properties of the nematocyst contents; this, when undiluted, i.e., in an undischarged nematocyst, stains darkly with picric acid or methylen blue; in successive stages of the eversion of the thread it stains successively lighter.

Von Lendenfeld, in reviewing this explanation of Iwanzoff's, says: "So schön diese Theorie auch ist, so erscheint sie doch ganz unhaltbar," the objections which he considers insurmountable being two:

1. The thin probably chitinous wall of the capsule could not possibly prevent the access of water to the intensely hygroscopic contents.
2. The fact that the contents of undischarged nematocysts are stained proves that water can enter without discharging them.

Also when a nematocyst is extruded from a cnidosac of an *Æolid*, as stated above, there is nothing there capable of removing the operculum. But, though the second objection seems fatal to Iwanzoff's theory as it stands, I think a slight modification of the same will not only avoid these difficulties but explain a number of facts inexplicable on any other hypothesis as yet propounded.

When we examine the conditions antecedent to the discharge of nematocysts in *Cœlenterates* and *Nudibranchs*, we find that apparently the only one common to the two cases is a change of the medium immediately surrounding the nematocyst. In *Cœlenterates* the nematocysts before discharge are partially protruded from the surface of the nematocytes into the surrounding water; in *Æolids* the nematocyst is extruded from the cnidosac into the water. The nematocysts of the *faeces* also discharge themselves on being extruded from the rectum into water. In each case it seems to be the passage from a solution of greater to one of less concentration which causes the eversion of the thread. This idea is confirmed by the following observations:—

1. In connection with the earlier part of this paper I had occasion to examine a large number of *Æolid* cerata for the identification and comparison of the nematocysts. For this purpose I found Calberla's fluid a very convenient examination medium; but though large numbers of nematocysts were usually extruded on placing the ceras in this liquid, the threads were never everted except when a large proportional amount of sea water was carried over with the ceras.
2. Similarly, if a ceras be examined in a fairly strong solution of sugar or salt, the nematocysts are not discharged, but if the

preparation be subsequently washed out with distilled water, the threads of the nematocysts are at once everted.

3. I have obtained similar results with Actinian tentacles. If a tentacle of an expanded Actinian is plucked off and plunged as quickly as possible into a 50-per-cent. concentrated solution of sugar, and then teased up, though many nematocysts are found discharged, it is quite easy to find pieces in which none are discharged. I have isolated such pieces, and after further teasing up, have kept them for periods varying from 24—72 hours. The nematocysts were always still undischarged, but when the sugar solution was washed out with water a certain number (never more than approximately 20 per cent.) discharged themselves. The fact that 80 per cent. did not discharge themselves is probably due to the presence of the other tissues of the tentacle preventing the access of the water, for in similar experiments with nematocysts from a ceras of an *Æolid*, the whole lot were discharged when washed out with water.

These facts seem to show that the discharge of a nematocyst is due to osmosis. The capsule apparently contains a solution of such a strength that it takes up water from such a weak solution as sea water, but not from the protoplasm of the nematocytes, or the fluids in the alimentary canal of *Æolids*, or from any of the other solutions mentioned above.

This hypothesis does away with the necessity of supposing the capsule wall to be impermeable, and so avoids Lendenfeld's first objection. As regards the second objection, it must be remembered that for a stain to reach an undischarged nematocyst it must pass through the protoplasm of the nematocyte; it diffuses into the layer of liquid immediately surrounding the nematocyst without appreciably altering the degree of concentration, therefore, without upsetting the balance between the liquids within and without the capsule, so that by diffusion in both directions the stain can enter the capsule without causing discharge. This applies to intra-vitam staining in *Cœlenterates*; fixing reagents probably so alter both capsule contents and protoplasm, and perhaps also capsule wall, that arguments based on the behaviour of fixed nematocysts are untrustworthy.

But though this hypothesis explains why nematocysts are not discharged while in the alimentary canal and cnidosacs of *Æolids*, and are discharged when extruded into the water, two other questions suggest themselves—

1. To what is the apparent immunity of *Æolids* towards the nematocysts of *Cnidaria* due?
2. How is it that we do not find in the cnidosacs a large number

of discharged nematocysts, used by their original owners in defence against the devouring *Æolids*?

1. We have seen that M. Hecht considered the immunity of *Æolids* towards the nematocysts of *Cœlenterates* to be in some way due to their possession of nematocysts of their own. But, of course, when the origin of the nematocysts of *Æolids* is known, it is obvious that this immunity is not a result, but a necessary condition of their possession.

Boutan (7) contends that the immunity of *Æolids* is not absolute, and that it is due at any rate in part to the secretion of mucus and the mode of attack. He dropped a healthy *Æ. papillosa* into the middle of the tentacles of an expanded actinian; the *Æolid* secreted large quantities of mucus, and after a short struggle escaped, and eventually devoured the actinian. Another individual of the same species, which had just been depositing ova and had so exhausted its supply of mucus, being treated in the same way as the last, was itself devoured. A third specimen, which had also been depositing ova, was simply placed in the same vessel with an actinian, which it devoured, beginning at the base of the column.

*Æ. papillosa* is, of course, an actinian-eating species and so accustomed to dealing with these animals. I have found *Spurilla neapolitana* to be equally capable of escaping from the clutches of an anemone. On the other hand, a particularly large and active specimen (6 cm. long) of *R. peregrina*, a species which usually feeds on hydroids, on being dropped among the tentacles of an expanded actinian, started to crawl out, but when the actinian began to envelope it with tentacles, it drew back and writhed in the centre, secreting mucus copiously and throwing off all its cerata. After several more vain attempts at escape it remained almost motionless, and would undoubtedly have been devoured had I not removed it with a pipette. The mucus was found to be crowded with the discharged nematocysts of the anemone and a few from the cnidosacs of the *Rizzolia*. The cast-off cerata were also pierced with the barbed threads of many actinian nematocysts. As for the *Æolid* itself, its tentacles and rhinophores, the anterior processes of the foot and the whole posterior part of the same, seemed quite paralysed, and remained stiff and useless for 3 or 4 days.

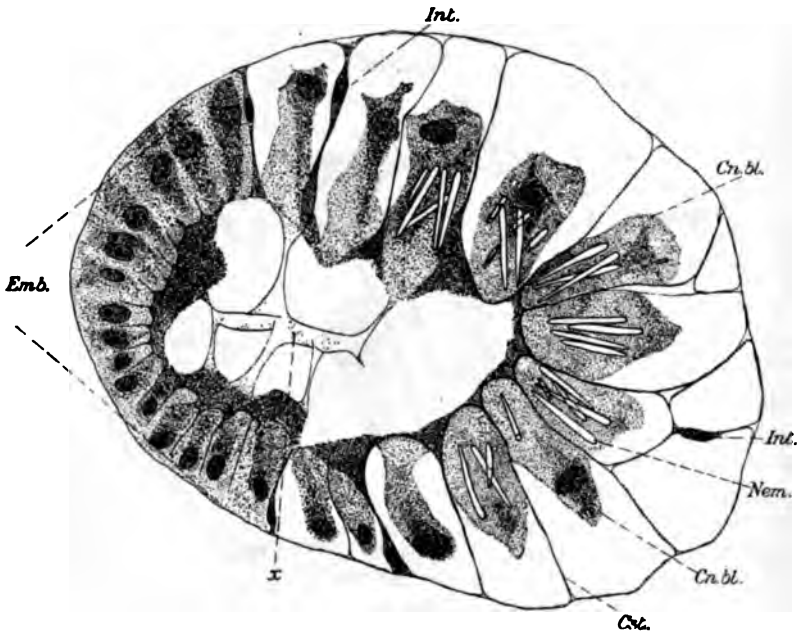
These experiments show not only that the immunity is by no means complete, but also that it depends on something besides a copious secretion of mucus.

2. The presence of only undischarged nematocysts in the cnidosacs of *Æolids* may be due to the nematocysts never having been discharged, or to the threads of discharged nematocysts having re-inverted by the action of the digestive fluids.

When a hydroid polyp is plucked off and examined in sea water the

small nematocysts of the tentacles usually remain undischarged; even the large nematocysts found at the base of the tentacles of many hydroids (*Eudendrium*) are often not discharged unless the polyps are teased up, compressed or otherwise stimulated. It is quite possible, therefore, that no attempt is made by the prey to discharge its nematocysts till it has been swallowed by the *Æolid* and immersed in juices of sufficient concentration to prevent the discharge. Perhaps a preliminary covering of mucus may help to delay the discharge.

FIG. 11.



On the other hand, since it is known that the thread of a developing nematocyst is formed outside the capsule and is only inverted when complete, presumably by the extraction of water from the capsule by the surrounding protoplasm, it is quite possible that the gastric juices of an *Æolid* may have the same effect on a discharged nematocyst.

#### *Development and Structure of the Cnidocysts.*

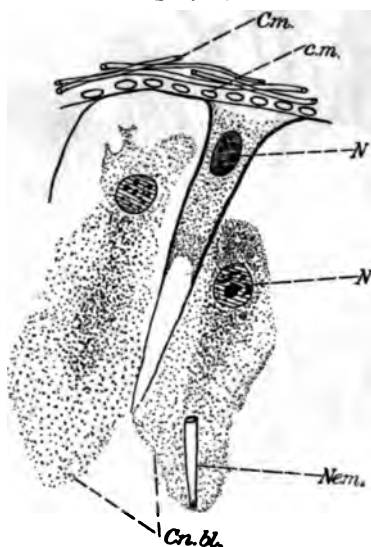
Thanks to Davenport, Hecht and Krembrow, the origin of the cnidosacs from the distal extremities of the ceratal diverticula of the gastric gland is thoroughly established, and the general outline of its development known. What observations, however, have been made on

the structure and development of the individual cnidocysts have, of course, been from the generally accepted point of view, *i.e.*, that they are nematocyst-secreting cells, instead of receptacles for fully formed foreign nematocysts.

The embryonic tissue of the cnidosac lies at the base, immediately surrounding the opening of the ciliated canal, and differentiation proceeds regularly from this point upwards, the oldest cnidocysts being next the external aperture. I have never observed a layer of embryonic cnidoblasts external to the fully formed ones.

From this embryonic zone, besides the cnidoblasts or central cells of each cnidocyst, there are developed certain interstitial cells which

FIG. 12.

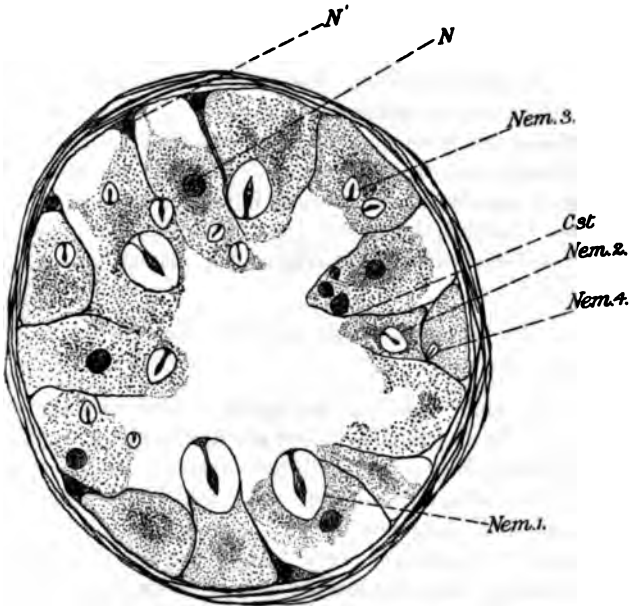


apparently take part in the secretion of the membranous cysts; these are perhaps what Herdman describes as young cnidoblasts. They lie at first between the bases of the cnidoblasts, from which they can be readily distinguished by their smaller size, and by the different staining reactions of their nuclei (fig. 12).

It is round this basal end of each cnidoblast that the membranous cyst is first secreted; the cnidoblast itself is drawn away from this point towards the lumen of the cnidosac, and does not apparently take part in the secretion of the cyst, but in the meantime ingests nematocysts at its opposite end, which remains naked and amoeboid. When sufficient nematocysts have been ingested and arranged by the cnidoblast, the membranous cyst is completed, the nuclei of the intermediate cells moving up between the cnidoblasts about half way towards the lumen

of the cnidosac. When the cyst is completed both the cnidoblast and the associated intermediate cells undergo degeneration, so that in the older parts of the cnidosac each cnidocyst consists simply of a membranous bag, containing nematocysts, which are often apparently attached to its inner wall to keep them in place, and a more or less degenerate cnidoblast; while wedged between adjacent cnidocysts are found small darkly staining bodies, the remains of the intermediate cells (fig. 13).

FIG. 13.



#### Summary.

The facts brought forward as evidence that the nematocysts of *Æolids* are derived from their prey are as follows:—

1. Not only are nematocysts of *Æolids* and *Cœlenterates* identical in plan of construction and mode of discharge, but each of several distinct types occurs in both groups.
2. A single type of nematocyst does not occur uniformly throughout a species, but different individuals of the same species may have quite different nematocysts; moreover, a single individual may have nematocysts of several different types, found in as many distinct species or groups of *Cœlenterates*.
3. When it is known on what *Cœlenterate* an *Æolid* has recently been feeding, the nematocysts of the two are found to be

identical. Also the nematocysts from the fæces of an *Æolid*, which are generally admitted to be derived from their food, are always identical with at least some of the nematocysts from the cnidosacs.

4. Those *Æolids* (*Janidæ*, *Fionidæ* and *Calma glaucoides*) which habitually feed on animals other than *Cœlenterates* have no nematocysts.
5. Though several have tried, no one has succeeded in giving even a plausible account of the development of nematocysts in *Æolids*.
6. This view affords a satisfactory explanation of the function of the ciliated canal through which nematocysts and other indigestible bodies have been observed to pass from the gastric diverticulum to the cnidosac.
7. A repetition of Strethill Wright's experiments gave entirely confirmatory results. In one case three *R. peregrinas*, having only small pip-shaped nematocysts in their cnidosacs, were fed on *Pennaria Cavolinii*, the nematocysts of which, after a month, had almost entirely replaced the original pip-shaped ones.

In Section III the functions of the nematocysts and cnidophores of *Æolids* are discussed :

There is little doubt that the borrowed nematocysts are used as defensive weapons by the *Æolids* ; they are discharged after extrusion from the cnidosacs ; they are usually so arranged in the cnidocysts that the threads are shot out radially ; the cerata are brightly coloured and are erected and elongated on the approach of a foreign body. The nematocysts are, however, very seldom ejected indiscriminately into the surrounding water, but usually only when the individual cerata are squeezed or plucked off.

The original and still important function of the terminal openings of the cerata is probably to allow of the escape of the nematocysts and other indigestible bodies, which, owing to the diffuse nature of the digestive cavity, it is impossible to eliminate entirely through the anus only.

*Mechanism of Nematocysts.*—The behaviour of nematocysts in *Æolids* proves that their discharge must be independent of the direct action of living tissue. The explanation most in accordance with the facts observed both under natural conditions and in experiments with various liquids and solutions, seems to be that the eversion of the nematocyst thread is due to the contents taking up water by osmosis from the surrounding sea water, but being unable to take it up from more concentrated solutions, such as the liquid surrounding the nematocysts in the *Cœlenterate* nematocyte or the digestive juices of *Æolids*.

The immunity of *Æolids* towards the nematocysts of Coelenterates is not complete. It is probably due largely to the secretion of mucus, which either acts simply as a shield, or actually prevents the discharge of nematocysts.

Even without the application of mucus, the nematocysts of a hydroid are often not discharged when a polyp is plucked off the stock, so that they may be swallowed by the *Æolid* intact. Or the gastric fluids which are strong enough not to give up water to an undischarged nematocyst, may extract water from a discharged one and so cause the reinversion of the thread.

*Development of Cnidocysts.*—The cnidocysts are derived each from two or more cells of two kinds; (a) a single cnidoblast or central cell which ingests and arranges the nematocysts; (b) an undetermined number of interstitial cells which probably secrete the membranous cyst. In the adult cnidocyst both kinds of cells undergo more or less degeneration, leaving practically only a membranous bag containing nematocysts.

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## EXPLANATION OF FIGURES.

- Fig. 1.—Small Pip-shaped Nematocysts of Tentacles of Eudendrium from Cnidosac of *Rizzolia peregrina*. × 560.
- „ 2.—Nematocysts of *Pennaria Carolinii*. × 560.
- „ 3.—Nematocysts of *Tubularia*. × 560.
- „ 4.—Large Bean-shaped Nematocysts from Body of Polyp of Eudendrium. × 560.
- „ 5.—Nematocysts from Cnidosacs of *Facelina punctata*, specimen B. × 900.
- „ 6.—Large oblong Nematocysts from *Flabellina affinis*. × 560.  
a. Tip of Basal portion of Thread. × 900.
- „ 7.—Nematocysts of *Aiptasia variabilis*. × 560.
- „ 8.—Actinian Nematocysts from Cnidosacs of *Spurilla neapolitana*. × 560.
- „ 9.—Nematocysts from young Specimen of *Spurilla neapolitana*. × 560.  
a. Ditto. × 900.
- „ 10.—Nematocysts from Cnidosac of *Aeolidiella Alderi*. × 560.  
a. From Acontia of *Sagartia*. b. From Tentacles of same.
- „ 11.—Oblique Section through young Cnidosac of *Spurilla neapolitana*. Stained with Ehrlich-Biondi. × 1360.  
*Emb.*, embryonic zone at base of cnidosac; *Cn. bl.*, cnidoblast; *Nem.*, nematocyst; *Ct.*, membranous cyst; *Int.*, interstitial cells, nuclei stained greenish; *Int.*', degenerate interstitial cell, nuclei stained red.
- „ 12.—Small Portion of another Section of the same Cnidosac.  
*Cn. bl.*, cnidoblasts; *N.*, nucleus of same, stained reddish; *N'*, nucleus of interstitial cell, stained green; *l. m.*, longitudinal muscles; *c. m.*, circular muscles; *Nem.*, nematocyst.
- „ 13.—Transverse Section through middle of a Cnidosac of *R. peregrina*, fed on *Pennaria Carolinii* for one month. Some of the cnidoblasts are already surrounded by membranous cysts, while others are still ingesting nematocysts. Stained with thionin. × 800.  
*Nem. 1.*, large nematocyst of *Pen. Carolinii* just being ingested.  
*Nem. 2.*, small „ „ stained reddish-violet.  
*Nem. 3.*, „ „ „ pale blue.  
*Nem. 4.*, „ Eudendrium nematocyst.

"On the Fructification of *Neuropteris heterophylla*, Brongniart."

By ROBERT KIDSTON, F.R.S., L. and E., F.G.S. Received  
November 17,—Read December 3, 1903.

(Abstract.)

This paper contains a description of three small specimens of *Neuropteris heterophylla*, Brongt., each of which shows a fragment of a terminal portion of a pinna bearing a large Rhabdocarpous seed, about 3 cm. long and from 1·10—1·40 cm. wide. Their general form is oblong, but they taper from the centre into a micropylar point. To the fragments of the stems is attached one—in one case two—pinnules, identical in form and nervation to those of *Neuropteris heterophylla*, Brongt. One of the specimens also shows a subtending bract-like leaf.

These specimens further show that the example previously described by the writer as the fructification of *Neuropteris heterophylla*, which also bore characteristic barren pinnules of that species, must be the "male inflorescence" of the plant, though the structure of the bodies supported on the naked dichotomous branchlets cannot be clearly made out. *Neuropteris heterophylla* is, therefore, a typical member of the Cycadofilices.

The specimens bearing the "seeds" came from the middle coal measures of the South Staffordshire coal field and are preserved in small ironstone nodules. They were communicated to the writer for examination by Mr. H. W. Hughes, F.G.S., Dudley.

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"Histological Studies on Cerebral Localisation." By ALFRED W. CAMPBELL, M.D. Communicated by Professor C. S. SHERRINGTON, F.R.S. Received November 17,—Read December 3, 1903.

(Abstract.)

*Introduction.*

The essential aim of this work is to further the establishment of a correlation between physiological function and histological structure.

The present communication deals with the central gyri, the occipital, temporal and limbic lobes; but an account of the remainder of the cortex, viz., that of the frontal and parietal lobes and the insula, will be presented to the Society at a later date.

*I.—Material and Methods.*

The normally existent topographic variations in arrangement of cortical nerve cells and medullated nerve fibres have been adopted as a standard criterion in forming judgment on points bearing on localisation, and a thorough examination of the disposition of these elements over the entire cortex of a series of human and anthropoid apes' brains constitutes the groundwork of the research; but, in addition to this, pathological material has been employed to amplify and confirm points concerning the topographic distribution of special areas, suggested in the first place by the normal arrangement.

*II.—General Histological Considerations.*

After some general explanatory remarks on medullated fibre arrangement and cell lamination, each definable cortical area is discussed in turn.

*III.—The Pre-central or Motor Area.*

The pre-central or motor type of cortex is confined—roughly speaking—to the pre-central or ascending frontal convolution and a small coterminous portion of the paracentral lobule, its distinctive histological characters are a wealth of nerve fibres far superior to that of any other part of the cerebral cortex, and the presence of the "giant cells" of Betz or "ganglionic cells" of Bevan Lewis. It is important to notice that its structure differs absolutely from that of the post-central or ascending parietal gyrus.

On examining the brains of two chimpanzees and one orang it was found that a similar area could be mapped out, not only agreeing closely in point of structure and distribution with that in the human

brain, but coinciding absolutely with the field which Sherrington and Grünbaum have recently found responsive to unipolar faradization in the same animals.

Strong confirmatory evidence in support of the assumption that in man, as well as in the man-like ape, the elements controlling volitional muscular movements reside in this area, is afforded by an examination of the brain in cases of Amyotrophic Lateral Sclerosis, a disease limited in its attack to the motor system of neurones. In two such brains submitted to exhaustive examination a wholesale disappearance of the "giant cells" of Betz from the whole of their normal area of occupation has been disclosed. In the same brains the post-central gyrus entirely escaped affection.

Valuable material for the determination of differential localization in the motor field is afforded by the brains of individuals who have been disabled by amputation of one or other extremity, for in due course, either as a result of section of the nerve fibres with which they stand connected, or of suppression of the energy which they elaborate, the cortical "giant cells" controlling muscles in the amputated member undergo the change "*réaction à distance*" (Marinesco). In three cases of amputation of the leg and a like number of cases of amputation of the arm, in which the central convolutions were converted into serial microscopic sections, alterations were discovered limited in distribution to fields agreeing closely with Sherrington and Grünbaum's respective leg and arm areas in the ape.

The annectant gyrus or buttress at the level of the superior genu, relatively barren in "giant cells," seems to be an important guide to the point where the trunk area intervenes between those of the arm and leg.

#### IV.—*Post-central and Intermediate Post-central Areas.*

This area is readily defined in both man and the man-like ape, and is limited in its distribution to the post-central or ascending parietal gyrus and its paracentral annexe, the floor of the fissure of Rolando forming a definite anterior boundary.

Since its cortical structure differs markedly from that of the motor area, and at the same time exhibits features common to known sensory areas (the visual and auditory), its supposed motor function is denied, and it is maintained on the following additional grounds that it constitutes the terminus where fibres conveying common sensory impressions primarily impinge. Physiologically it is "silent" under the influence of electrical excitation, and also partial ablations give rise to no interference with movement (Sherrington and Grünbaum). Its fibres, like those of sensory spinal tracts, myelinate early (Flechsig and Vogt). It is the terminus for the "cortical lemniscus" (Tschermak).

Personal observations in three cases of *Tabes Dorsalis*, a disease affecting the sensory system of neurones essentially, have disclosed profound cortical alterations concentrated in this area. Similar observations in cases of amputation of an extremity have revealed changes situated on a corresponding surface level with those noted in the pre-central or motor area.

It is suggested that confusion concerning the function of the central gyri has arisen in the past, from the fact that the tracts of fibres pertaining to these gyri run in such close association below the Rolandic floor, that a lesion affecting the conduction chain of one gyrus is rarely free from the damaging influence of involvement of the other.

*Intermediate Post-central Area.*—This is a skirting zone in which the structural type is intermediate between that of the post-central area and the remaining parietal gyri.

It may serve for the transmutation and further elaboration of impressions primarily received in the post-central area.

#### V.—*Visual Area.*

*Calcarine or Visuo-Sensory Area.*—Two definite and distinct areas each possessing a specialised type of cortex can be mapped out in the occipital lobe. The distribution of the first is influenced by and bears an extremely close relation to the calcarine fissure; for the histologist its chief feature is the well-known line of Gennari.

Strong grounds exist for believing that this field is designed for the primary reception of visual sensations, and of these the following may be mentioned; the only fibres in the occipital lobe possessing a myelinic investment at the period of full foetal maturation are those proceeding to this area (Flechsig); clinico-pathologists have proved that the minimal lesion equivalent to the production of a maximum of blindness is one concentrated in the calcarine region; it is possible to map out this area from changes in it occurring as a result of old-standing blindness (Bolton).

*Occipital or Visuo-Psychic Area.*—The second definable area forms an investing zone or skirt to the first, and a remarkable wealth of nerve fibres coupled with the presence of curious large pyramidal cells serve for its identification. It is argued that this cortex is specialised for the final elaboration and interpretation of sensations first received as crude impressions in the calcarine area, and that its destruction is responsible for those disabilities included in the category of psychic blindness.

In the chimpanzee and orang analogous areas can be demonstrated, but they extend much more widely on the lateral surface of the hemisphere.

VI.—*Temporal Lobe.*

*Audito-Sensory Area.*—The first important field is a small one occupying the transverse temporal gyri, and therefore concealed within the Sylvian fissure. As this is the first temporal cortex to become medullated, as it seems to be the terminus of the central auditory tract, and as there are clinico-pathological reasons for believing that its destruction is equivalent to the production of complete deafness, the assumption is favoured that it constitutes the primary auditory centre. But further evidence on this point is needed, and the results of the examination of the part in cases of congenital or long-standing deafness of peripheral origin would be welcome.

*Audito-Psychic Area.*—This area, of ready definition, covers the posterior three-fifths of the first temporal gyrus and is thus closely related to the one just mentioned. It is seen to correspond with the well-known centre for word-deafness, but in reference to that disability it must be indicated that the structure of this region is alike in the two hemispheres, and without denying the dominant psychic action of the area in the left hemisphere the opinion is expressed that the right side shares that function, because in the only recorded cases of complete, uncomplicated and irrecoverable word-deafness, verified by an autopsy—there are but two—a bilateral lesion has been discovered.

Similar areas are defined with equal readiness in the anthropoid brain.

*Common Temporal Area.*—The remainder of the temporal cortex shows a uniform type of structure stamped by a poverty in fibres and cells of large size, and it has been disappointing to discover that the angular gyrus is not endowed with any specialised arrangement.

VII.—*Limbic Lobe.*

*Pyriform or Olfactory Area.*—Histology supports comparative anatomy in suggesting that the lobus pyriformis must be regarded as the principal cortical centre, although not the sole one, governing the olfactory sense. Remarkable superficially-placed clusters of large stellate cells and a tendency on the part of the projection fibres to gain the surface, characterise its structure, and the rudimentary fissura rhinica forms a most definite limit.

*Hippocampal Area and Cornu Ammonis.*—The cortex covering the wall and lip of the fissura hippocampi differs from the above and also from that of the gyrus dentatus, but the function of this part remains obscure.

*Limbic Area.*—This practically covers the whole gyrus fornicatus. In the pregenual part deep chromophilous cells may be seen, resem-

bling ones found in the lobus pyriformis, and it seems likely that these are the end-stations for fibres proceeding from the inner olfactory root.

A total absence of large fibres and large cells and a simple plan of arrangement is the general character of this area and does not lend colour to the doctrine that it, and not the Rolandic region, is a centre for common sensation.

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“On the Integrals of the Squares of Ellipsoidal Surface Harmonic Functions.” By G. H. DARWIN, F.R.S., Plumian Professor and Fellow of Trinity College, Cambridge. Received December 2,—Read December 10, 1903.

(Abstract.)

This paper is a sequel to three others on ellipsoidal harmonic analysis and its applications, published in Series A of the ‘Philosophical Transactions,’ vol. 197, pp. 461—557; vol. 198, pp. 301—331; and vol. 200, pp. 251—314.

The integrals referred to in the title are absolutely essential for practical applications of this method of analysis. A table of all such integrals is given in the first of the above-named papers, but the results are only approximate. In the present paper the rigorous forms of the integrals, numbering  $1 + 3 + 5 + 7$ , are given for the surface harmonics of orders 0, 1, 2, 3.

A mistake is detected on p. 556 of the first of the previous papers, where the coefficient of  $\beta$  in the cosine-function of the third zonal harmonic is erroneously given as 3; it should have been  $\frac{5}{2}$ .

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"Preliminary Note on the Resistance to Heat of *B. anthracis*." By  
A. MALLOCK, F.R.S., and Lieut.-Col. A. M. DAVIES, R.A.M.C.,  
Received November 30,—Read December 10, 1903.

Very discrepant statements have been made by various authorities as to the degree of temperature and duration of heating requisite to destroy the spores of various species of bacteria. The great importance of the subject, especially as regards the rapid and effective sterilisation of water for troops in the field, made us think it worth while to undertake the experiments here recorded.

Our object was to determine a curve whose ordinates should represent the time necessary for sterilisation in terms of the temperature to which the infected water was heated. Since many of the authorities give very long times as necessary (ranging from 10 minutes to some hours) even at temperatures considerably above 100° C., we expected to find that the slope of the curve would be a comparatively gentle one, and would meet the temperature axis at a finite but acute angle. This expectation, however, was not fulfilled, and we rarely found any survival of living matter in fluid which had been raised to a temperature of 100° C. even for as short a time as 20—30 seconds.

In our earlier experiments (Nos. 1—85) we used *B. anthracis*, *B.m. ruber*, *Staph. p. aureus*, *Staph. p. citreus* and *B. subtilis*, but subsequently we confined our attention to anthrax, and the results here recorded refer only to this latter, which may be considered as a typically resistant germ.

The experiments consisted in exposing infected water in sealed glass tubes to heat in steam, at various temperatures, and for various times, the contents of the tubes being afterwards incubated in broth.

The method and procedure employed is described in some detail, so that there may be no doubt about the conditions under which the results were obtained.

The heat was applied in a small closed chamber (A) (fig. 1), which by means of a two-way cock (B) could be placed in communication either with a steam boiler, or with the outer air.

The chamber had an easily removable steam-tight cover, to which was attached a light brass holder (C) fitted to receive six of the culture tubes.

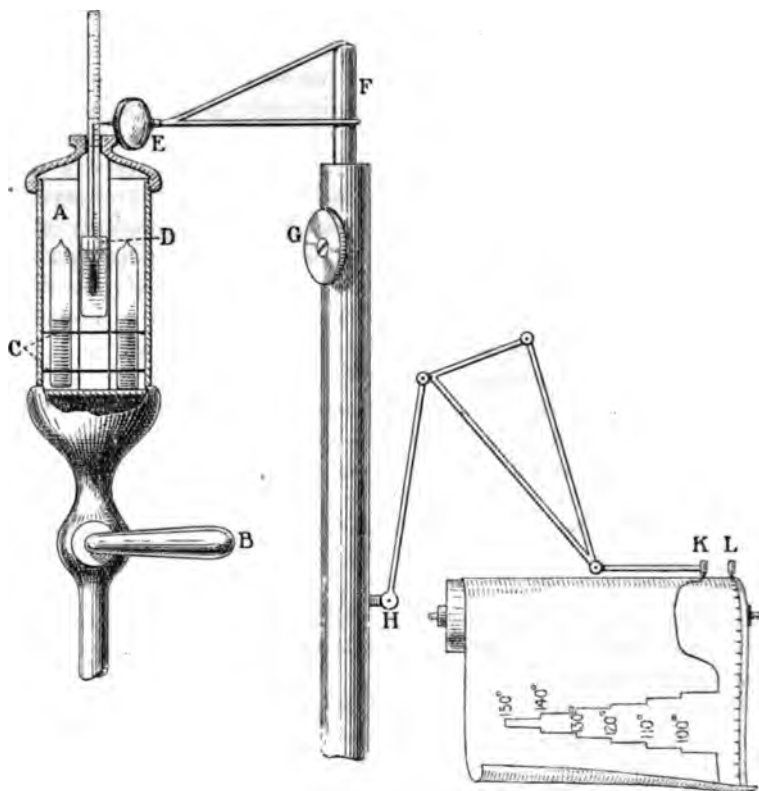
Through the centre of the cover a thermometer was introduced into the chamber, its stem passing through a steam-tight packing, and its bulb dipping into water contained in the glass tube (D), of the same size as the culture tubes. The stem of the thermometer outside the chamber could be viewed through a lens attached to a movable pointer (E). This pointer was carried on the vertical rod (F), which could be moved up and down by the milled head (G), and a pen (K), connected



by levers with the rod at (H), marking on uniformly moving paper, indicated the position of the pointer at each instant. Time was also recorded on the paper by means of another pen (L) worked from an electric clock beating seconds.

During an experiment the pointer was kept carefully on the end of the mercury column in the thermometer, so that the diagram on the paper gave the temperature of the tubes in terms of time.

FIG. 1.



The tube in which the thermometer bulb dipped had the same amount of water in it, to start with, as was contained in the culture tubes, but as the thermometer tube was open to the steam in the chamber, and the culture tubes were sealed, the water in the former would acquire the temperature of the steam more rapidly than the liquid in the culture tubes. Thus the temperature to which the cultures were exposed must have been a little less than that recorded, but only when the times of heating were very short would the difference be appreciable.

The actual procedure in all the experiments was as follows:—Sterilised glass tubes 3 inches long and  $\frac{1}{2}$  inch diameter were about half filled with infected water, and the tubes were then sealed with the blow-pipe. This was effected without warming the contents by placing the tubes upright in a holder revolved by clockwork at about thirty revolutions per minute; the top of the tube was then heated by an upward pointing flame until its diameter contracted to about  $\frac{1}{4}$  inch, and drawn to a point by means of a previously heated glass tube held in the hand.

The tubes were next placed in the holder attached to the cover of the chamber, the water in the tube surrounding the thermometer was brought to the same temperature as the sealed tubes and the cover placed on the heating chamber. Before admitting steam, however, the paper record was started and the pointer (E) brought successively to 90°, 100°, 110°, 120°, 130°, 140°, 150°, on the thermometer scale, so that each record might have on it a thermometer scale for reference. Steam was then admitted and the requisite temperature maintained for the time determined on. With a little practice in manipulating the two-way cock it was found easy to keep the temperature constant within a quarter of a degree Centigrade. Of course the temperature which it was wished to maintain was settled beforehand, but in the results the temperatures are taken from the records.

The method of inoculating the tubes was as follows:—The tubes, having been plugged and sterilised by dry heat, were half filled with distilled water, re-plugged, and then sterilised in the steamer for half an hour on three successive occasions. On the morning of the day of experiment the tubes were inoculated with the respective organisms, either from an agar or broth culture, as stated in each instance, and again plugged. Within two or three hours the inoculated tubes were sealed up and submitted to the different degrees and durations of heat, as detailed in the table. This having been done, the tops of the tubes were filed off, and the contents sown into broth with the least possible delay, generally within two hours. Microscopic examination of the culture inoculated was made in each case immediately before sowing into the tubes; and afterwards, as soon as growth (if any) made its appearance in the inoculated broth, in order to verify the purity of the cultures.

Care was taken in all cases to be sure that spores were present in the infected water.

The original growth of *Bacillus anthracis* was obtained from a pure culture on agar, supplied by the kindness of Dr. J. W. H. Eyre, Bacteriologist to Guy's Hospital; this was derived from the blood of a fatal case of anthrax in the wards of the Hospital in March, 1903. Sub-cultures were made from this strain, and inoculated into the tubes of water, as detailed in the tables.

The following appearances were relied on, as indicating the growths of *B. anthracis* :—

*Nutrient Broth at 37° C.*—After 24—48 hours, whitish deposit, and presence of small flocculent masses in upper part of tube, which fall down on shaking; the broth itself remains clear; absence of any pellicle.

*Agar Stroke at 37° C.*—Whitish thin defined growth along the stroke, with irregular edges, not spreading widely.

*Microscopic Appearances.*—Rods, threads and felted masses, with spores either free or lying within the rods. Rods non-motile.

The subjoined table gives the results of all the experiments made on anthrax.

#### Experiments on *B. anthracis*.

| Date.   | Series. | Exp. | Culture. |         | Heated. |       | Results after incubation at 37°. |
|---------|---------|------|----------|---------|---------|-------|----------------------------------|
|         |         |      | In.      | Age of. | To.     | For.  |                                  |
|         |         |      |          | days.   | °C.     | m. s. |                                  |
| 1903.   |         |      |          |         |         |       |                                  |
| June 11 | I       | 1    | A*       | 3       | 104·5   | 5 0   | No growth.                       |
|         |         | 2    | B†       | 2       | 104·5   | 5 0   | "                                |
| " 16    | II      | 6    | A        | 7       | 104·5   | 5 0   | "                                |
|         |         | 7    | B        | 6       | 104·5   | 5 0   | Contaminated growth.             |
|         |         | 8    | B        | 3       | 104·5   | 5 0   | Some growth.                     |
| " 19    | III     | 13   | B        | 6       | 110·0   | 5 0   | No growth.                       |
|         |         | 14   | B        | 6       | 110·0   | 5 0   | Contaminated.                    |
| " 19    | IV      | 19   | B        | 6       | 115·0   | 5 0   | No growth.                       |
|         |         | 20   | B        | 3       | 115·5   | 5 0   | "                                |
| " 26    | V       | 25   | A        | 2       | 110·5   | 5 0   | Contaminated.                    |
|         |         | 26   | B        | 2       | 110·5   | 5 0   | No growth.                       |
| " 26    | VI      | 31   | A        | 2       | 110·5   | 2 30  | "                                |
|         |         | 32   | B        | 2       | 110·5   | 2 30  | "                                |
| July 2  | VII     | 37   | A        | 8       | 110·5   | 2 30  | "                                |
|         |         | 38   | B        | 8       | 110·5   | 2 30  | "                                |
| " 2     | VIII    | 43   | A        | 8       | 115·5   | 2 30  | "                                |
|         |         | 44   | B        | 8       | 115·5   | 2 30  | "                                |
| " 15    | IX      | 49   | A        | 21      | 115·5   | 2 30  | "                                |
|         |         | 50   | B        | 36      | 115·0   | 2 30  | "                                |
| " 15    | X       | 55   | A        | 21      | 117·0   | 1 0   | "                                |
|         |         | 56   | B        | 36      | 117·0   | 1 0   | "                                |
| " 22    | XI      | 61   | A        | 27      | 118·0   | 1 0   | "                                |
|         |         | 62   | B        | 42      | 118·0   | 1 0   | "                                |
| " 22    | XII     | 67   | A        | 27      | 116·0   | 0 30  | "                                |
|         |         | 68   | B        | 42      | 116·0   | 0 30  | "                                |
| " 29    | XIII    | 73   | A        | 35      | 116·0   | 0 30  | "                                |
|         |         | 74   | B        | 50      | 116·0   | 0 30  | "                                |
| " 29    | XIV     | 79   | A        | 35      | 114·0   | 0 20  | "                                |
|         |         | 80   | B        | 50      | 112·5   | 1 0   | "                                |
| Aug 12  | XV      | 85   | B        | 29      | 112·5   | 1 0   | "                                |
|         |         | 86   | B        | 29      | 112·5   | 1 0   | "                                |
| " 12    | XVI     | 87   | B        | 29      | 111·0   | 2 0   | "                                |
|         |         | 88   | B        | 29      | 111·0   | 2 0   | "                                |

\* A stands for agar. † B for broth.

| Date.    | Series. | Exp. | Culture. |         | Heated. |        | Results after incubation at 37°. |
|----------|---------|------|----------|---------|---------|--------|----------------------------------|
|          |         |      | In.      | Age of. | To.     | For.   |                                  |
| 1903.    |         |      |          | days.   | °C.     | m. s.  |                                  |
| Aug. 12  | XVII    | 89   | B        | 29      | 114·0   | 0 10   | No growth.                       |
|          |         |      |          |         | 107·0   | 0 50   |                                  |
|          |         | 90   | B        | 29      | 114·0   | 0 10   | "                                |
|          |         |      |          |         | 107·0   | 0 50   |                                  |
| " 12     | XVIII   | 91   | B        | 29      | 107·0   | 1 0    | "                                |
|          |         | 92   | B        | 29      | 107·0   | 1 0    |                                  |
| " 12     | XIX     | 93   | B        | 29      | 104·0   | 1 0    | "                                |
|          |         | 94   | B        | 29      | 104·0   | 1 0    |                                  |
| " 12     | XX      | 95   | B        | 29      | 102·0   | 1 0    | "                                |
|          |         | 96   | B        | 29      | 102·0   | 1 0    |                                  |
| " 18     | XXI     | 97   | B        | 35      | 110·5   | 0 20   | Slight growth.                   |
|          |         | 98   | B        | 35      | 110·5   | 0 20   |                                  |
| " 18     | XXII    | 99   | B        | 35      | 101·5   | 0 20   | No growth.                       |
|          |         | 100  | B        | 35      | 101·5   | 0 20   |                                  |
| " 18     | XXIII   | 101  | B        | 35      | 101·5   | 0 12   | "                                |
|          |         | 102  | B        | 35      | 101·5   | 0 12   |                                  |
| " 18     | XXIV    | 103  | B        | 35      | 100·0   | 1 0    | "                                |
|          |         | 104  | B        | 35      | 100·0   | 1 0    |                                  |
| " 18     | XXV     | 105  | B        | 35      | 100·0   | 0 20   | "                                |
|          |         | 106  | B        | 35      | 100·0   | 0 20   |                                  |
| " 18     | XXVI    | 107  | B        | 35      | 100·0   | 2 0    | "                                |
|          |         | 108  | B        | 35      | 100·0   | 2 0    |                                  |
| Sept. 24 | XXVII   | 109  | B        | 6       | 99·0    | 5 0    | Slight growth.                   |
|          |         | 110  | B        | 6       | 99·0    | 5 0    |                                  |
| " 24     | XXVIII  | 111  | B        | 6       | 99·0    | 4 0    | No growth.                       |
|          |         | 112  | B        | 6       | 99·0    | 4 0    |                                  |
| " 24     | XXIX    | 113  | B        | 6       | 99·0    | 3 0    | "                                |
|          |         | 114  | B        | 6       | 99·0    | 3 0    |                                  |
| " 24     | XXX     | 115  | B        | 6       | 100·0   | 5 0    | "                                |
|          |         | 116  | B        | 6       | 100·0   | 5 0    |                                  |
| " 24     | XXXI    | 117  | B        | 6       | 100·0   | 2 0    | "                                |
|          |         | 118  | B        | 6       | 100·0   | 2 0    |                                  |
| " 24     | XXXII   | 119  | B        | 6       | 100·0   | 1 0    | "                                |
|          |         | 120  | B        | 6       | 100·0   | 1 0    |                                  |
| " 30     | XXXIII  | 121  | A        | 45      | Not     | heated | Copious growth, contaminated.    |
|          |         | 122  | A        | 45      | "       | "      |                                  |
| " 30     | XXXIV   | 123  | A        | 45      | 100·0   | 5 0    | Copious growth of anthrax.       |
|          |         | 124  | A        | 45      | 100·0   | 5 0    |                                  |
| " 30     | XXXV    | 125  | A        | 45      | 100·0   | 2 30   | Copious growth, not anthrax.     |
|          |         | 126  | A        | 45      | 100·0   | 2 30   |                                  |
| " 30     | XXXVI   | 127  | A        | 45      | 100·0   | 1 0    | Contaminated growth.             |
|          |         | 128  | A        | 45      | 100·0   | 1 0    |                                  |
| " 30     | XXXVII  | 129  | A        | 45      | 99·0    | 5 0    | "                                |
|          |         | 130  | A        | 45      | 99·0    | 5 0    |                                  |
| " 30     | XXXVIII | 131  | A        | 45      | 99·0    | 2 30   | "                                |
|          |         | 132  | A        | 45      | 99·0    | 2 30   |                                  |
| Oct. 7   | XXXIX   | 133  | A        | 52      | 101·0   | 2 30   | No growth.                       |
|          |         | 134  | A        | 52      | 101·0   | 2 30   |                                  |
| " 7      | XL      | 135  | A        | 52      | 101·0   | 1 0    | Contaminated.                    |
|          |         | 136  | A        | 52      | 101·0   | 1 0    |                                  |

| Date.  | Series. | Exp. | Culture. |         | Heated. |       | Results after incubation at 37°. |
|--------|---------|------|----------|---------|---------|-------|----------------------------------|
|        |         |      | In.      | Age of. | To.     | For.  |                                  |
| 1903.  |         |      |          | days.   | °C.     | m. s. |                                  |
| Oct. 7 | XLI     | 137  | A        | 52      | 101·0   | 1 0   | No growth.                       |
|        |         | 138  | A        | 52      | 101·0   | 1 0   | "                                |
| " 7    | XLII    | 139  | A        | 52      | 105·0   | 1 0   | Contaminated.                    |
|        |         | 140  | A        | 52      | 105·0   | 1 0   | No growth.                       |
| " 7    | XLIII   | 141  | A        | 52      | 105·0   | 0 30  | Contaminated.                    |
|        |         | 142  | A        | 52      | 105·0   | 0 30  | No growth.                       |
| " 7    | XLIV    | 143  | A        | 52      | 105·0   | 0 12  | Contaminated.                    |
|        |         | 144  | A        | 52      | 105·0   | 0 12  | No growth.                       |
| " 14   | XLV     | 145  | A        | 5       | 100·0   | 2 30  | "                                |
|        |         | 146  | A        | 5       | 100·0   | 2 30  | "                                |
| " 14   | XLVI    | 147  | A        | 5       | 100·0   | 1 0   | "                                |
|        |         | 148  | A        | 5       | 100·0   | 1 0   | "                                |
| " 14   | XLVII   | 149  | A        | 5       | 100·0   | 0 20  | "                                |
|        |         | 150  | A        | 5       | 100·0   | 0 30  | "                                |
| " 14   | XLVIII  | 151  | A        | 5       | 101·0   | 2 30  | "                                |
|        |         | 152  | A        | 5       | 101·0   | 2 30  | "                                |
| " 14   | XLIX    | 153  | A        | 5       | 101·0   | 1 0   | "                                |
|        |         | 154  | A        | 5       | 101·0   | 1 0   | "                                |
| " 14   | L       | 155  | A        | 5       | 103·0   | 0 30  | "                                |
|        |         | 156  | A        | 5       | 103·0   | 0 30  | "                                |
| " 22   | LI      | 157  | A        | 8       | 99·5    | 0 20  | "                                |
|        |         | 158  | A        | 8       | 99·5    | 0 20  | "                                |
| " 22   | LII     | 159  | A        | 8       | 101·0   | 0 30  | "                                |
|        |         | 160  | A        | 8       | 101·0   | 0 30  | "                                |
| " 22   | LIII    | 161  | A        | 8       | 99·8    | 10 0  | "                                |
|        |         | 162  | A        | 8       | 99·8    | 10 0  | "                                |
| " 22   | LIV     | 163  | A        | 8       | 99·5    | 5 0   | "                                |
|        |         | 164  | A        | 8       | 99·5    | 5 0   | "                                |
| " 22   | LV      | 165  | A        | 8       | 102·0   | 0 30  | "                                |
|        |         | 166  | A        | 8       | 102·0   | 0 30  | "                                |
| " 22   | LVI     | 167  | A        | 8       | 103·0   | 0 25  | "                                |
|        |         | 168  | A        | 8       | 103·0   | 0 25  | "                                |

It will be seen that in all 113 experiments were made; of these 95 were at temperatures above 100° C. and 18 below.

Out of the 95, 14 cases occurred in which some growth took place after incubation. In 12 cases out of the 14 the growth was contaminated.

Out of the 18 experiments below 100° C., growth occurred in 5 cases, in only 1 of which (viz., in Experiment 109) was a pure Anthrax developed.

Whether Anthrax was really present in any of the contaminated growths is somewhat doubtful. All that can be said is that in 3 cases the usual *Subtilis* contamination was accompanied by a non-motile spore-bearing bacillus growing in threads, which, as far as appearance goes, might be Anthrax.

Looking at the experiments as a whole, and considering that ten

different sub-cultures were experimented with at many different ages, and that in only two cases (viz., Experiments 8 and 97) was a pure Anthrax growth obtained when the infected water had been raised to 100° C., we conclude that any heating of Anthrax spores in water to this or any higher temperature, even for the shortest practicable time, is almost certain to insure their destruction.

What is the lower limit of destructive temperature, when the heating is prolonged, we have not attempted to determine, but we hope to make some observations on this point both with regard to Anthrax and some other spore-bearing bacilli, and to give the results in a further communication.

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“On the Resemblances Exhibited between the Cells of Malignant Growths in Man and those of Normal Reproductive Tissues.”\*

By J. BRET LAND FARMER, F.R.S., J. E. S. MOORE, F.L.S., and C. E. WALKER. Received December 8,—Read December 10, 1903.

The object of this communication is to draw attention to certain important cytological transformations exhibited during the development of malignant growths in man. We believe that the changes we are about to describe are diagnostic of malignant as opposed to those of a benign character. Furthermore, if our conclusions are well founded, they may at the same time serve to throw light upon the nature of the processes involved in the formation of these growths, and we hope that they may also serve as a point of departure for further investigations on the more remote aetiology of the disease itself.

We wish, however, at the outset, to disclaim all intention of formulating at the present time any theory as to the nature of these various remote causes, although, as will be seen in the sequel, our observations indicate certain directions along which such causes may perhaps be profitably sought.

We may at once state as the results of our investigations on a large number of malignant growths, including numerous examples of *Carcinomata* and *Sarcomata*, that we have been able to trace in detail a number of definite and serial changes in the cells of the invading and proliferating malignant tissue, which are remarkably similar to those obtaining during the maturation of the elements contained within the sexual reproductive glands, and it would seem that such a resemblance,

\* We desire to state that whilst working together at this subject we have each approached the problems from an independent standpoint. The paper is in every sense a joint one.

extending as it does to minute points of detail, can hardly be destitute of grave significance.

In order, however, to make the position clear, it will be necessary briefly to consider the essential features in which the gametogenic\* tissues which are destined to become the reproductive elements are found to differ from the other elements or cells of which the body or soma of an animal or plant is elsewhere composed.

When the egg of an animal or a plant segments to give rise to an organism, the nuclei of all the resulting cells are found to contain a definite number of chromosomes during each nuclear division. These chromosomes pass through a constant series of evolutionary changes. At first the material out of which they originate appears as an aggregation of granules of a stainable substance (chromatin) which finally gives rise to definite structures, the chromosomes. These latter are constant in number for each species of animal or plant, and each of them divides longitudinally into two daughter-chromosomes.

The chromosomes at this period of division become arranged in a very definite manner on the spindle, frequently appearing as V's with the apex directed towards the axis of the spindle. The daughter-nuclei are formed by the distribution to either pole of the respective halves of each original chromosome, and the nuclei thus formed may then enter on a condition of complete rest. Whenever new somatic cells are formed in the body the nuclei pass through identically similar phases. But in every individual there are certain gametogenic cells that are destined to give rise, not to the specialised tissues, but to the sexual reproductive elements. Such cells may be differentiated at a very early period in the embryonic ontogeny of the organism, or they may only become recognisable at a later stage. At whatever stage they may be formed, however, their further history is entirely different from that of the surrounding somatic tissues. The difference in question first becomes apparent as the cell commences its preparation for division, and it is distinguished both by its highly peculiar appearance, and by the fact that at a definite stage in the multiplication of the cells of this reproductive tissue, each unit that is about to give rise to actual reproductive cells passes through a series of metamorphoses wholly dissimilar from those of the surrounding tissues as well as of those of the antecedent cells by the division of which such a cell has sprung. To the peculiar form of mitosis associated with this metamorphosis the term *heterotype* has been applied, and it is a characteristic and interpolated stage in the reproductive cycle of all sexually propagating higher animals and plants.

\* The term *gametogenia*, as here proposed, is also intended to include the primary sporogenous tissue of plants; in spite of possible objections that may be raised, we have decided on this course to secure consistency of expression. [Note added December 16, 1903.]

The essential features wherein this heterotype mitosis differs from those of the body or soma of the organism (whether plant or animal), as well as those in the cell-generations of the reproductive tissues that have preceded it, are as follows :—

1. The period of rest and growth.
2. The chromosomes where they are formed from the resting nucleus are present in only *half the number* of those occurring in the rest of the dividing nuclei of the organism.
3. The forms exhibited by these chromosomes are strikingly different from those of other nuclei. They produce figures resembling loops, rings, aggregations of four heads, and so on.
4. Their division on the spindle is transverse and not longitudinal.

It will be thus seen that this heterotype mitosis is an easily recognised phase in the history of the development of the sexual cells, and for our purpose this is the essential point. With its theoretical interpretation we are not here concerned.

But it is a fact of the highest importance that when once the heterotype division has supervened, all the descendants of that cell retain the reduced number of chromosomes in normal cases. The cycle of these cell-generations, the nuclei of which only forms half the somatic number of chromosomes, normally closes with the formation of the definite sexual cells. It is on the fusion of two of these (ovum and spermatozoon) that the double or somatic number is restored, and this number is characteristic of the fertilised egg, and of all the cells to which it gives rise, until the heterotype mitosis again supervenes in the reproductive tissues. Now after the intervention of the heterotype division, the cell in which it has occurred may, after one further division, at once give birth to the four sexual cells, as in the higher animals, or, on the other hand, a varying number of cell-generations may be intercalated before the final differentiation of the sexual elements. This occurs in the majority of plants. It is in these latter that the commonly parasitic character of the organism thus arising is specially, though not exclusively, apparent. Thus, the embryo sac of many flowering plants exerts a destructive influence on the cells of the soma adjacent to it. This property is not, however, by any means exclusively confined to the post-heterotype formation (the gametophyte of the plant), and we do not wish to lay distinctive weight upon it. In the lower plants the bulk of the body is composed of cells with reduced nuclei, and the alternate stage in the life cycle, originating in the fertilised egg, is the predatory structure. What seems to emerge from a general consideration of the whole range of facts is this : that in the higher animals and plants the post-heterotype tissue, with its own independence of organisation, does behave towards the surrounding tissues of the parental individual as a neoplasm. So far as the parent is concerned, the new growth might be described



as a pathological one, did it not form a normal stage of the life-history of the species.

We have said that the cells from which the heterotypically dividing elements will finally arise can often be distinguished from those cells which will not produce such elements. In the testis of a mammal or in the sporogenous tissue of a stamen we recognise with ease and certainty the existence of these cells. They continue to multiply, and though differing from the adjacent cells in many respects, they continue to resemble them in their mode of nuclear division until they pass severally into the peculiar state of growth that ushers in the heterotype division.

In our studies of abnormal growths occurring on ferns, we were struck by certain features presented by the proliferating tissues that are formed during apogamy and apospory, and we have thus been led to make a systematic investigation of the cytological features presented by malignant growths in man.

This has resulted in the recognition of the existence of a surprising degree of similarity between the phases that characteristically recur in such tissues and those transformations of somatic cells into reproductive tissues in general.

Thus in a typical example of rapidly growing epithelioma it is seen that in the early stages of the proliferation of the Malpighian layer, the cells of the invading tissue at first pass through a cycle of somatic divisions, exactly as in the early stages of reproductive tissue. The resemblance may extend to the frequent production of giant cells, a common occurrence in each case.

As cell multiplication proceeds, however, a change passes over the cells themselves. The protoplasmic continuity, to which the "prickly" character is due, becomes more or less obliterated, and the cells assume that appearance of indifferent germ tissue so well known as a feature of the elements of which malignant growths are largely made up. But, in addition to this, other important changes occur which seem to have been generally overlooked.

A varying number of cells, situated in a zone behind the growing edge of the advancing neoplasm, may be observed to attain somewhat large dimensions. Each contains a nucleus that grows to a considerable size. As the latter enters on a prophase of division, it is recognised that the chromosomes, instead of appearing as delicate thin rods or V's, which are split longitudinally, present the appearance of short thickened loops or rings, closely resembling the later prophase stages of the heterotype mitosis in the normal reproductive tissues. What is still more significant is the fact that in these cells the number of the chromosomes is obviously *less than* in the *normal somatic cells of the surrounding tissues*. In many cases we determined the numbers to be approximately halved as compared with those of the

latter. Furthermore, it is clear that the loops and rings characteristic of this stage of the cellular development of the malignant growth are arranged lengthwise on the spindle, and so are ultimately divided transversely, exactly as in the corresponding heterotype mitosis of the reproductive elements.

Subsequent divisions that occur behind this zone appear to resemble the somatic form, but retain a reduced number of chromosomes, just as do the cells that arise from a parent cell that has once exhibited the heterotype character. But irregularities of various kinds usually supervene—amitosis is of frequent occurrence, and the number of the chromosomes in those nuclei that may continue to divide mitotically often exhibits irregularity. These facts do not, however, seriously affect our position, for in many plants similar irregularities occur in post-heterotype cells that are not destined to give rise to actual sexual cells.

The above-described series of cellular and nuclear changes are not confined to epitheliomata, but recur in an essentially similar manner in other carcinomata and sarcomata. For example, in a rapidly developing growth of a sarcomatous type from the *cervix uteri* we were able to distinguish near the growing edge a well-marked zone of cells, characterised by the somatic (and amitotic?) types of mitosis, whilst this was succeeded towards the interior by a band of heterotypically dividing cells, and within this again the cells showed the somatic type with reduced number of chromosomes, together with other cells in which a mitosis was going on.

In the case of slow-growing tumours which obviously tend to produce a considerable amount of normal somatic tissue, such as the fibrous tissue in scirrhus of the breast, cells showing these phases are, as would naturally be expected, far more difficult to find than in rapidly growing tumours. In such growths, cells showing the figures of ordinary somatic division are numerous in comparison with those showing heterotype figures. This would seem to indicate that the cells which are destined to form fibrous tissue never divide heterotypically.

It thus becomes evident that in a most important respect the various types of malignant growths present certain features which are common to all, and that these features are similar to those to be observed in the process of differentiation of reproductive cells from the preceding somatic tissue. We feel that the evidence justifies us in deliberately correlating the appearance of these "gametoid" neoplasms with the result of a stimulus which has changed the normal somatic course of cell development into that characteristic of reproductive (not embryonic) tissue.

We look, then, upon this transformation as representing the immediate cause of the development of the malignant growth but

the remote cause must be sought for amongst those various stimuli, some of which, *e.g.*, continuous irritation, are known to favour their development.

Malignant growths seem, furthermore, to be definitely separable from benign tumours, inasmuch as in the latter we have never succeeded in discovering anything resembling the very characteristic nuclear changes we have described above. Thus, *inter alia*, while we have in the example of a polypoid papilloma observed a considerable number of somatic mitoses with the full (unreduced) number of chromosomes, we have been wholly unable to find a single instance of a heterotype division, or anything indicating that a reduction in the number of chromosomes had taken place.

In this preliminary communication we do not propose to deal, except in the most brief manner, with such questions as the probable transmission of the disease from one individual to another, or to its prevalence in certain districts, or even in certain houses.

It seems probable that actual contact does in some cases transmit the disease, but it is apparently equally probable that this happens where cells from the growth are transplanted to another part of the same individual, or to another individual under very peculiar conditions, which allow of the repeated application of a suitable stimulus, or of the continuous introduction of cells which have undergone the changes we have described.

In the case of localities where malignant growths are apparently prevalent, *e.g.*, cancer houses, the phenomenon is directly comparable to the occurrence of abnormal cellular developments under suitable stimuli to which we have already referred.

In conclusion we would point out that the various changes which we have described as occurring in cells are always rapid, and possibly hastened during the approaching death of the tissue. Unless, therefore, the tissues are treated in such a manner as to fix the cells composing them some time before death supervenes, the nuclei will be found either in a condition of rest or in one of more or less disintegration. We have emphasised this fact because, in the ordinary pathological methods of preparing specimens, it has not hitherto been found necessary to make proper provision for the preservation and fixation of the cells, either with regard to time or suitable reagents. Such preparations, though, of course, admirably suited for ordinary histological investigation, are not suitable for elucidation of the finer cytological characters of the individual cells.

We cannot bring this communication to a close without expressing our great indebtedness to Dr. W. R. Dakin and to Messrs. Allingham, Baldwin, English, Jaffery, Parsons, Shield, and others, who, by so kindly enabling us to obtain the necessary material, have made this investigation possible.

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"Mathematical Contributions to the Theory of Evolution. XII.  
—On a Generalised Theory of Alternative Inheritance, with  
Special Reference to Mendel's Laws." By KARL PEARSON,  
F.R.S. Received September 11,—Read November 26, 1903.

(Abstract.)

(1). A great deal of interest has been recently excited by Mendelian theories of inheritance, and a considerable amount of controversy has arisen with regard to their relation to the statistical treatment of inheritance within large populations. The fundamental conception of the Mendelian theory is the non-fusion of the gametes of two pure races on crossing. If  $A, A'$  represent the pure gametes of one race and  $a, a'$  those of the other, the individual arising from the zygote formed by crossing these races contains not fused gametes, but pure gametes of the two original races, and these gametes are equally represented on further crossings among the hybrids. The whole may be exhibited symbolically as

$$(AA') \times (aa') = (A + A')(a + a') = (Aa) + (Aa') + (A'a) + (aa'),$$

where in the first product we have the parental zygotes; in the second product the breaking-up into the gametes is indicated, and on the extreme right the zygotes of the resulting offspring are given. This is a perfectly simple conception. We can generalise it at once by replacing the simple couplet  $(AA')$  by  $n$  such couplets, and supposing the original parental zygotes to be of the form

$$(A_1A_1) + (A_2A_2) + (A_3A_3) + \dots + (A_nA_n),$$

$$(a_1a_1) + (a_2a_2) + (a_3a_3) + \dots + (a_na_n),$$

where each corresponding pair of couplets on crossing obeys the above symbolic formula. If two individuals, constituted as above, be crossed, they give a generation of hybrids. If these hybrids now breed at random and are equally fertile among themselves, segregation takes place. If the process of random mating with equal fertility be continued generation by generation, what further changes, if any, take place, and what are the laws of inheritance within such a population? This is the general problem I have set myself to attack by mathematical analysis. I speak of it as a generalised theory of alternative inheritance; it is based on a pure gamete conception. It is not Mendelian in so far as it replaces his simple couplet by  $n$ -couplets, and supposes the character determined by these  $n$ -couplets and not a single couplet. Further, it entirely dispenses with Mendel's fundamental ideas of recessive and dominant characters. To avoid any such assumption I speak of the protogenic and allogenic couplets  $(aa')$  and  $(AA')$ . I take

the character to be fixed in some way by the number of protogenic or allogenic couplets in the constitution of the individual zygote. It would have been equally easy to fix it by the heterogenic couplets. My object is to discover the chief features of heredity in a population breeding at random under a generalised system of pure gametes, and to determine how far the results are in accordance with the biometric experience of what happens in such populations.

I am quite aware that my theory, although far more general than Mendel's, is not the most general which might be propounded. A whole crop of Mendelian formulæ have been proposed for isolated special cases by various writers. But I venture to think that this has been done with a certain want of scientific responsibility. Their authors do not seem to have realised that every such formula involves absolutely rigid laws for inheritance within a population mating at random, and that before such formulæ are propounded, a research ought to be made as to what general laws of heredity flow from them and whether such laws are in accordance with existing experience. The present memoir will indicate that to follow up one such general Mendelian theory requires a great deal of mathematical labour, and that in future the onus of testing the generality of a Mendelian formula propounded to account for some single hybridisation result ought to fall on its propounder.

What the present investigation does demonstrate is this, that the most general theory of the pure gamete hitherto developed leads to broad features of inheritance, which are in perfect accord with the biometric theory of inheritance in populations. Nor, if this theory of the pure gamete were correct, is there anything to be surprised at in the result. The biometric theory is purely a statistical description based upon experience and is not dependent upon any physiological hypothesis. On the other hand, any physiological hypothesis applied to heredity must fall if it does not accord with the results obtained by observations on such populations.

(2). Developing the theory described above we find :—

(a). That segregation occurs when the hybrids cross.

(b). That when the members of this segregating generation cross at random the population accurately reproduces itself, and supposing no artificial, natural or reproductive selection to take place, a stable population or "race" is created, which is permanent and shows a permanent proportional frequency for each sub-class of the population. There is no room for further segregation or for "mutations" as long as this state of affairs is maintained. Any selection, however, would at once produce a progressive change in the population.

(c). The regression of the offspring on any ancestor whatever is linear.

(d). The ancestral correlations form a geometrical series. The

results (a) to (d) involve what I have termed the law of ancestral heredity, which is thus seen to hold for a general population obeying the most general theory of the pure gamete hitherto developed mathematically.

(e). The distribution of the population itself follows a skew binomial law, which approaches closer and closer to the Gaussian distribution as we increase the number of couplets in the constitution of the zygote. All these results are in broad agreement with what biometric investigations have shown us to hold for the inheritance and distribution of frequency in populations.

(3). We now turn to points of divergence :—

(f). The parental correlation is  $\frac{1}{2}$ .

(g). The ratio of diminution of ancestral correlation at each stage is  $\frac{1}{2}$ .

(h). The correlation between brothers is sensibly 0·4.

One-third is the value originally given by Francis Galton for parental correlation ;  $\frac{1}{2}$  is the value of the ratio of ancestral diminution which really follows from his geometrical series  $\frac{1}{4}$ ,  $\frac{1}{8}$ ,  $\frac{1}{16}$ , etc., for ancestral contributions, and 0·4 is the corresponding value of fraternal correlation.\*

The generalised Mendelian theory thus fixes absolutely inheritance for all characters in all races, *i.e.*, inheritance is no function of the number of couplets determining the constitution. These results, while in accordance with Galton's original views, do not seem in accordance with more recent statistical observations on populations.

The value for parental correlation is not constant either for character or species ; it varies sensibly, and it clusters about a value 0·45 to 0·5, sensibly higher than the value  $\frac{1}{2}$  above given. The value for fraternal correlation is, indeed, somewhat larger than that for parental correlation, but it clusters about a value 0·5 to 0·6, and is sensibly higher than the value 0·4 obtained from this Mendelian theory. The values  $\frac{1}{6}$ ,  $\frac{1}{12}$ ,  $\frac{1}{24}$ , found for grandparental, great grandparental and great great grandparental correlations from this theory are all very sensibly less than the values actually obtained from observation. The ratio of diminution is more nearly  $\frac{2}{3}$  than  $\frac{1}{2}$ .

Hence, this Mendelian generalisation fails when we test it by actual numbers.

(4). Points of theoretical divergence, not depending upon numerical measures, are the following :

(i). If  $p$  be the number of allogenic couplets in the father,  $q$  in the mother, the number  $m_{pq}$  to be expected on the average in the offspring is given by

$$m_{pq} = \frac{1}{n} \frac{(n+2p)(n+2q)}{n} \dots\dots\dots (i)$$

\* 0·4 and not  $\frac{2}{3}$  as in " Natural Inheritance " is the value for fraternal correlation which flows from Galton's hypothesis, see ' Roy. Soc. Proc., ' vol. 62, p. 410.

on the generalised pure gamete theory ; and by

$$m_{pq} = \frac{1}{12}n + \frac{1}{3}(p+q) \dots\dots\dots (ii)$$

on the theory of linear regression.

In other words, regression holds for the great bulk of a Mendelian population, but grows gradually less as we treat the matings of nearly pure allogenic parents, ceasing entirely with absolutely pure allogenic parents. When  $n = 5$ , a mating between pure allogenic parents occurs only once in a million matings. If we limit our attention to 99 per cent. of the population, even when  $n$  is comparatively small, we find regression on the mid-parent sensibly given by the Galtonian theory of the midparent, and when  $n$  is anything at all considerable, the Galtonian theory gives the value of the average offspring sensibly correct for 999 in 1000 of the population, becoming absolutely correct as  $n$  is indefinitely increased. The theory of regression shows us that the planes (ii) are the best fitting planes to the hyperboloids (i), and this fit becomes better and better as  $n$  becomes larger.

Except for very small values of  $n$ , it would probably be impossible to get an accurate test of the truth of the theory of the pure gamete by using formula (i) ; the errors of random sampling are for the great bulk of the population as large as the divergence between (i) and (ii).

(j). If a correlation table for parents and offspring be formed in a Mendelian population, while the regression will be real and linear, the variability of the number of allogenic couplets in the array of offspring due to a parent of definite allogenic constitution will steadily increase if we pass from the pure protogenic to the pure allogenic parent. The mean variability of the arrays of offspring is equal to  $\sigma\sqrt{(1-r^2)}$ , where  $\sigma$  is the variability of the general population, and  $r$  the coefficient of parental correlation. This mean value exactly agrees with that given by statistical theory. But no one has hitherto observed this gradual change of variability in the arrays as we pass across a parental correlation table. It is not very marked, especially when  $n$  is large, and may, perhaps, have escaped notice ; still one would be rather surprised if it had. This change of variability of arrays of offspring seems to provide a method of finding  $n$  the number of couplets in the constitution of the zygote. This point will doubtless receive attention, and there is ample material already collected to test it upon.

(k). The frequency of an array of offspring due to a given parent depends upon the product of two skew binomials. Whether there is approach to any skew, or normal curve, when  $n$  is increased has not yet been investigated, but the deviation from normality exhibited would on the surface appear to be considerable, and such deviation would be inconsistent with the approximately elliptic contour lines which have been noted by Galton in discussing human characters.

(5). To sum up: The memoir shows that any physiological hypothesis, such as a generalised theory of the pure gamete, is not *à priori* inconsistent with the broad conceptions of linear regression, parental correlation, ancestral influence, and with the distribution of frequency actually observed in populations. The theory under discussion, indeed, leads to these results, and they have only escaped the Mendelians because they did not develop their formulæ for the case of a population crossing at random, but confined their attention too much to the hybridisation of pure races, and to self-fertilising individuals. On the other hand, there are marked numerical divergences between the results observed for populations and those deduced from the generalised theory of the pure gamete, which seem to definitely prevent its acceptance as a general theory of heredity. It would be of very great value to have a physiological theory which would not only lead up to the general laws of inheritance—involved in the principles of regression and of ancestral influence—this is actually achieved by the present theory—but which would also lead to numerical results in reasonable accord with experience. Such a theory will, no doubt, be discovered in time, but the touchstone of its truth will be that it gives, not only a formula which does not vary from one simple case of crossing to a second, but also general principles and numerical values in accordance with those which have been observed for large populations, whether they breed at random, or exhibit homogenic tendencies. I think we are justified in asking any future propounder of Mendelian formulæ to apply this touchstone, and to remember that the statistical view of inheritance is not at basis a theory, but a description of observed facts, with which any physiological theory must be in accord.

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## INDEX to VOL. LXXII.

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- Ætolds*, nematocysts of (Grosvenor), 462.
- Aitken (J.) On the Formation of Definite Figures by the Deposition of Dust, 211.
- Alcock (N. H.) On the Rapidity of the Nervous Impulse in Tall and Short Individuals, 414.
- Alloys of aluminium and tin (Anderson and Lean), 277.
- Alternating-current machines, "hunting" of (Hopkinson), 235.
- Aluminium-tin alloys, properties of (Anderson and Lean), 277.
- Anderson (H. K.) See Hardy and Anderson.
- Anderson (W. C.) and Lean (G.) The Properties of the Aluminium-Tin Alloys, 277.
- Apes, physiology of cortex of (Grünbaum and Sherrington), 152.
- Arcs, spectra of metallic, in exhausted globe (Fowler and Payn), 253.
- Armstrong (H. E.) and Lowry (T. M.) The Phenomena of Luminosity, and their possible Correlation with Radio-activity, 258.
- B. anthracis*, resistance to heat of (Mallock and Davies), 493.
- Bactericidal action of ultra-violet radiations (Barnard and Morgan), 126.
- Bainbridge (F. A.) On the Adaptation of the Pancreas to different Food-stuffs, 35.
- Baly (E. C. C.) The Spectra of Neon, Krypton, and Xenon, 84.
- Barnard (J. E.) and Morgan (H. de R.) Upon the Bactericidal Action of some Ultra-violet Radiations as produced by the Continuous-current Arc, 126.
- Barratt (J. O. W.) Note on the Disintegration of Rabid Brain Substance, 35f
- Beam of rectangular section, solution for bending of (Filon), 391.
- Beilby (G. T.) Surface Flow in Crystalline Solids under Mechanical Disturbance, 218; — The Effects of Heat and of Solvents on Thin Films of Metal, 226.
- Betaine, action of, on nerve and heart (Waller and Sowton), 320; (Waller and Plimmer), 345.
- Bevan (P. V.) The Combination of Hydrogen and Chlorine under the Influence of Light, 5.
- Bottomley (W. B.) and Jackson (Herbert) Some Preliminary Observations on the Assimilation of Carbon Monoxide by Green Plants, 130.
- Boulenger (G. A.) On Reptilian Remains from the Trias of Elgin, 55.
- Buchanan (J. Y.) On a Remarkable Effect produced by the Momentary Relief of Great Pressure, 88.
- Campbell (A. W.) Histological Studies in Cerebral Localisation, 488.
- Carbon-dioxide assimilation, effect of temperature on (Matthaei), 355.
- Carbon monoxide, assimilation by green plants (Bottomley and Jackson), 130.
- Cells of malignant growths and of normal reproductive tissues (Farmer, Moore, and Walker), 499.
- Cerebral cortex of anthropoids, physiology of (Grünbaum and Sherrington), 152.

- Cerebral localisation, histological studies in (Campbell), 488.
- Chalmers (S. D.) The Theory of Symmetrical Optical Objectives, 267.
- Chloroform, use of, in preparation of vaccine (Green), 1.
- Choline, action of, on nerve and heart (Waller and Sowton), 320.
- Chree (C.) An Analysis of the Results from the Kew Magnetographs on *Quiet Days* during the Eleven Years 1890—1900, with a Discussion of Certain Phenomena in the Absolute Observations, 22.
- Condenser moving in space, forces acting on (Trouton and Noble), 132.
- Convoluta Roscoffensis*, bionomics of (Gamble and Keeble), 93.
- Covariant of system of binary forms, maximum order of (Young), 399.
- Crookes (Sir W.) The Ultra-violet Spectrum of Radium, 295, 413; — and Dewar (Jas.) Note on the Effect of Extreme Cold on the Emanations of Radium, 69.
- Croonian Lecture (Timiriazeff), 424.
- Cullum (J. E.) Mean Results of Monthly Determinations of the Magnetic Elements at the Valencia Observatory, Cahirciveen, 211.
- Cyanogenesis in plants (Dunstan and Henry), 285.
- Cyanophyceæ, cell structure of (Wager), 401.
- Darwin (G. H.) On the Integrals of the Squares of Ellipsoidal Surface Harmonic Functions, 492.
- Davies (A. M.) See Mallock and Davies.
- Dewar (James) See Crookes and Dewar.
- Diffraction des ondes électriques (Poincaré), 42.
- Diffusion of salts in solution, measurement of (Graham), 212.
- Dines (W. H.) See Shaw and Dines.
- Douglas (S. R.) See Wright and Douglas.
- Dunstan (W. R.) and Henry (T. A.) Cyanogenesis in Plants. Part III.—On Phaseolunatin, the Cyanogenetic Glucoside of *Phaseolus lunatus*, 285.
- Dust-figures formed by deposition (Aitken), 211.
- Earthquake phenomena and elastic theory (Lamb), 128.
- Elasmometer, new form of elasticity apparatus (Tutton), 193.
- Electricity, discharge of, from hot platinum (Wilson), 272.
- Ellipsoidal surface harmonic functions (Darwin), 492.
- Evaporation of water in a current of air (Perman), 72.
- Evolution, mathematical contributions to theory of (Pearson), 505.
- Farmer (J. B.) and Moore (J. E. S.) New Investigations into the Reduction Phenomena of Animals and Plants.—Preliminary Communication, 104; — and Walker (C. E.) On the Resemblances exhibited between the Cells of Malignant Growths in Man and those of normal Reproductive Tissues, 499.
- Fats, hydrolysis of, by means of steapsin (Lewkowitsch and Macleod), 31; synthesis during absorption (Moore), 134.
- Filon (L. N. G.) On an Approximate Solution for the Bending of a Beam of Rectangular Cross-section under any System of Load. Additional note, 391.
- Forsyth (A. R.) The Differential Invariants of Space, 294.
- Fossils, investigation by serial sections (Sollas), 98.
- Fowler (A.) and Payn (H.) The Spectra of Metallic Arcs in an Exhausted Globe, 253.
- Fox (C. J.) See Travers and Fox.

- Gadow (H.) Evolution of the Colour-pattern and Orthogenetic Variation in certain Mexican Species of Lizards, with Adaptation to their Surroundings, 109.
- Gamble (F. W.) and Keeble (F.) The Bionomics of *Convolvula Roscoffensis*, with special Reference to its Green Cells, 93.
- Gamgee (A.) and Jones (Walter) On the Optical Activity of the Nucleic Acid of the Thymus Gland, 100.
- Gold leaf, structure of, and absorption spectrum of gold (Mallet), 68.
- Graham (J. C.) On the Measurement of the Diffusion of Salts in Solution, 212.
- Gray (Andrew) and Stewart (Walter) On the Radiation of Helium and Mercury in a Magnetic Field, 16.
- Green (A. B.) Preliminary Note on the Use of Chloroform in the Preparation of Vaccine, 1.
- Grosvenor (G. H.) On the Nematocysts of *Æolids*, 462.
- Grünbaum (A. S. F.) and Sherrington (C. S.) Observations on the Physiology of the Cerebral Cortex of the Anthropoid Apes, 152.
- Hardy (W. B.) and Anderson (H. K.) On the Sensation of Light produced by Radium Rays, and its Relation to the Visual Purple, 393; — and Willcock (E. G.) On the Oxidising Action of the Rays from Radium Bromide as shown by the Decomposition of Iodoform, 200.
- Helium, production of, from radium (Ramsay and Soddy), 204; radiation of, in a magnetic field (Gray and Stewart), 16.
- Henry (T. A.) See Dunstan and Henry.
- Hopkinson (B.) The "Hunting" of Alternating-current Machines, 235.
- Huggins (Sir Wm. and Lady) On the Spectrum of the Spontaneous Luminous Radiation of Radium at Ordinary Temperatures, 196; Further Observations on the Spectrum of the Spontaneous Luminous Radiation of Radium at Ordinary Temperatures, 409.
- Hydrogen and chlorine, combination of, under influence of light (Bevan), 5.
- Hydrophidæ, physiological action of poison of (Rogers), 305.
- Inheritance, theory of alternative, with reference to Mendel's law (Pearson), 505.
- Invariants, differential, of space (Forsyth), 294.
- Jackson (Herbert) See Bottomley and Jackson.
- Jones (Walter) See Gamgee and Jones.
- Keeble (F.) See Gamble and Keeble.
- Kew magnetographs, analysis of results from, 1890—1900 (Chree), 22.
- Kidston (R.) On the Fructification of *Neuropteris heterophylla*, Brongniart, 487.
- Kites, meteorological observations by use of (Shaw and Dines), 13.
- Krypton, spectrum of (Baly), 84.
- Lamb (Horace) On the Propagation of Tremors over the Surface of an Elastic Solid, 128.
- Lean (Geo.) See Anderson and Lean.
- Lewkowsitch (J.) and Macleod (J. J. R.) The Hydrolysis of Fats *in vitro* by means of Steapsin, 31.
- Light and combination of hydrogen and chlorine (Bevan), 5.
- Lizards, evolution of colour-patterns in certain (Gadow), 109.
- Lowry (T. M.) See Armstrong and Lowry.
- Luminosity, possible correlation with radio-activity (Armstrong and Lowry), 253.
- Lymph in tissues, measurement of (Oliver), 52.

- Macdonald (H. M.) The Bending of Electric Waves round a Conducting Obstacle: Amended Result, 59.
- Macleod (J. J. R.) See Lewkowitsch and Macleod.
- Magnetic elements, Valencia Observatory (Cullum), 211.
- Magnetic expansion of less magnetic metals (Shaw), 370.
- Magnetograph results at Kew, 1890—1900 (Chree), 22.
- Makower (W.) and Noble (H. R.) On the Measurement of the Pressure Coefficient of Oxygen at Constant Volume and different Initial Temperatures, 379.
- Malignant growths in man, cells of, compared with normal reproductive tissues (Farmer, Moore, and Walker), 499.
- Mallet (J. W.) On the Structure of Gold Leaf and the Absorption Spectrum of Gold, 68.
- Mallock (A.) and Davies (A. M.) Preliminary Note on the Resistance to Heat of *B. anthracis*, 493.
- Matthaei (G. L. C.) On the Effect of Temperature on Carbon-dioxide Assimilation, 355.
- Mendel's law and theory of alternative inheritance (Pearson), 505.
- Mercury, radiation from, in a magnetic field (Gray and Stewart), 16.
- Metal, effects of heat and solvents on thin films of (Beilby), 226.
- Metals, magnetic expansion of less magnetic (Shaw), 370.
- Meteorological observations by use of kites (Shaw and Dines), 13.
- Meyer (Hans) and Ransom (F.) Researches on Tetanus.—Preliminary Communication, 26.
- Moore (Benj.) On the Synthesis of Fats accompanying Absorption from the Intestine, 134.
- Moore (J. E. S.) See Farmer and Moore, and Farmer, Moore, and Walker.
- Morgan (H. de R.) See Barnard and Morgan.
- Muscarine, action of, on nerve and heart (Waller and Sowton), 320.
- Neon, spectrum of (Baly), 84.
- Nervous impulse, rapidity of, in tall and short people (Alcock), 414.
- Neuropteris heterophylla*, fructification of (Kidston), 487.
- Noble (H. E.) See Makower and Noble, and Trouton and Noble.
- Nucleic acid of thymus gland, optical activity of (Gamgee and Jones), 100.
- Oliver (G.) The Measurement of Tissue Fluid in Man. Preliminary note, 52.
- Optical objectives, theory of symmetrical (Chalmers), 267.
- Oxygen, measurement of pressure coefficient of (Makower and Noble), 379; vapour pressures of liquid (Travers and Fox), 386.
- Palaeospondylus Gunnii*, account of (Sollas and Sollas), 98.
- Pancreas, adaptation to different food-stuffs (Bainbridge), 35.
- Payn (H.) See Fowler and Payn.
- Peachey (S. J.) See Pope and Peachey.
- Pearson, (K.) Mathematical Contributions to the Theory of Evolution. XII.—On a Generalised Theory of Alternative Inheritance, with Special Reference to Mendel's Law, 505.
- Perman (E. P.) The Evaporation of Water in a Current of Air, 72.
- Phagocytosis, rôle of blood fluids in connection with (Wright and Douglas), 357.
- Phaseolunatin, cyanogenetic glucoside (Dunstan and Henry), 285.
- Photo-electric discharge from metallic surfaces (Varley), 11.
- Plant, cosmical functions of the green (Timiriuzeff), 424.
- Plants, assimilation of carbon monoxide by (Bottomley and Jackson), 130.
- Plimmer (R. H. A.) See Waller and Plimmer.

- Poincaré (H.) Sur la Diffraction des Ondes Électriques : à propos d'un Article de M. Macdonald, 42.
- Poison of the Hydrophidæ, physiological action of (Rogers), 305.
- Pope (W. J.) and Peachey (S. J.) A New Class of Organo-Tin Compounds containing Halogens, 7.
- Poynting (J. H.) Radiation in the Solar System: its Effect on Temperature and its Pressure on Small Bodies, 265.
- Pressure, effect of momentary relief of (Buchanan), 88.
- Rabid brain substance, disintegration of (Barratt), 353.
- Radiation in solar system, temperature and pressure effects (Poynting), 265.
- Radiation of helium and mercury in a magnetic field (Gray and Stewart), 16.
- Radiations, ultra-violet, effect on bacteria (Barnard and Morgan), 126.
- Radio-activity, experiments in (Ramsay and Soddy), 204; correlation with luminosity (Armstrong and Lowry), 258.
- Radium bromide, oxidising action of rays from (Hardy and Willcock), 200.
- Radium emanation, effect of extreme cold on (Crookes and Dewar), 69.
- Radium, intensely penetrating rays of (Strutt), 208.
- Radium, production of helium from (Ramsay and Soddy), 204.
- Radium rays, the sensation of light produced by (Hardy and Anderson), 393.
- Radium, spectrum of radiation of (Huggins and Huggins), 198, 409.
- Radium, ultra-violet spectrum of (Crookes), 295, 413.
- Ramsay (Sir W.) and Soddy (F.) Experiments in Radio-activity, and the Production of Helium from Radium, 204.
- Ramsden (W.) Separation of Solids in the Surface-layers of Solutions and "Suspensions." Preliminary account, 156.
- Ransom (F.) See Meyer and Ransom.
- Rayleigh (Lord) On the Bending of Waves round a Spherical Obstacle, 40.
- Reduction phenomena of animals and plants (Farmer and Moore), 104.
- Refraction in gases, theory of (Walker), 24.
- Reptilian remains from Trias of Elgin (Boulenger), 55.
- Rogers (L.) On the Physiological Action of the Poison of the Hydrophidæ. Part II.—Action on the Circulatory, Respiratory, and Nervous Systems, 305: On the Physiological Action and Antidotes of Colubrine and Viperine Snake Venoms, 419.
- Schmitz (H. E.) On the Determination of Specific Heats, especially at Low Temperatures, 177.
- Schott (G. A.) Note on Calculation of Magnetic Elongation of Cylindrical Bars, 375.
- Schunck (C. A.) The Xanthophyll Group of Yellow Colouring Matters, 165.
- Shaw (P. E.) The Magnetic Expansion of some of the Less Magnetic Metals, 370.
- Shaw (W. N.) and Dines (W. H.) Meteorological Observations obtained by the Use of Kites off the West Coast of Scotland, 1902, 13.
- Sherrington (C. S.) See Grünbaum and Sherrington.
- Snake venoms, physiological action and antidotes of (Rogers), 419.
- Soddy (F.) See Ramsay and Soddy.
- Sollas (W. J.) A Method for the Investigation of Fossils by Serial Sections, 98; — and Sollas (I. B. J.) An Account of the Devonian Fish, *Palæospondylus Gunnii*, Traquair, 93.
- Solution, measurement of diffusion of salts in (Graham), 212.
- Solutions and "suspensions," separation of solids in surface-layers of (Ramsden), 156.

- Sowton (S. C. M.) See Waller and Sowton.  
 Specific heats, determination at low temperatures (Schmitz), 177.  
 Steapsin, hydrolysis of fats by means of (Lewkowitch and Macleod), 31.  
 Stewart (Walter) See Gray and Stewart.  
 Strutt (R. J.) On the Intensely Penetrating Rays of Radium, 208.  
 Surface flow in crystalline solids (Beilby), 218.
- Tetanus, researches on (Meyer and Ransom), 28.  
 Timiriazeff (C.) The Cosmical Functions of the Green Plant (Croonian Lecture), 424.  
 Tin, organo-compounds of, containing halogens (Pope and Peachey), 7.  
 Travers (M. W.) and Fox (C. J.) The Vapour Pressures of Liquid Oxygen on the Scale of the Constant-volume Oxygen Thermometer filled at different Initial Pressures, 386.  
 Tremors, propagation of, over surface of elastic solid (Lamb), 128.  
 Trouton (F. T.) and Noble (H. R.) The Forces acting on a Charged Condenser moving through Space, 132.  
 Tutton (A. E. H.) The Elasmometer, a New Interferential Form of Elasticity Apparatus, 193.
- Vaccine, use of chloroform in preparation of (Green), 1.  
 Valencia observatory magnetic elements (Cullum), 211.  
 Vapour pressure of water—density of saturated vapour (Perman), 72.  
 Variation, orthogenetic, in certain Mexican lizards (Gadow), 109.  
 Varley (W. M.) On the Photo-electric Discharge from Metallic Surfaces in different Gases, 11.
- Wager (H.) The Cell Structure of the Cyanophyceæ.—Preliminary Paper, 401.  
 Walker (C. E.) See Farmer, Moore, and Walker.  
 Walker (G. W.) On the Theory of Refraction in Gases, 24.  
 Waller (A. D.) and Plimmer (R. H. A.) The Physiological Action of Betaine extracted from Raw Beet-Sugar, 345; — and Sowton (S. C. M.) The Action of Choline, Neurine, Muscarine, and Betaine on Isolated Nerve and upon the Excised Heart, 320.  
 Waves, bending of, round a spherical obstacle (Rayleigh), 40; (Poincaré), 42; (Macdonald), 59.  
 Waves, surface, and tremors in elastic solid (Lamb), 128.  
 Willcock (E. G.) See Hardy and Willcock.  
 Wilson (H. A.) On the Discharge of Electricity from Hot Platinum, 272.  
 Wright (A. E.) and Douglas (S. R.) An Experimental Investigation of the *Rôle* of the Blood Fluids in connection with Phagocytosis, 357.
- Xanthophyll group of colouring matters (Schunck), 165.  
 Xenon, spectrum of (Baly), 84.
- Young (A.) The Maximum Order of an Irreducible Covariant of a System of Binary Forms, 399.
- Zeeman effect on radiation from helium and mercury (Gray and Stewart), 16.

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